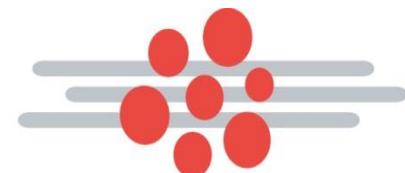


X-ray Photoelectron Spectroscopy for Chemical Analysis

J. ANIBAL BOSCOBOINIK

jboscoboinik@bnl.gov

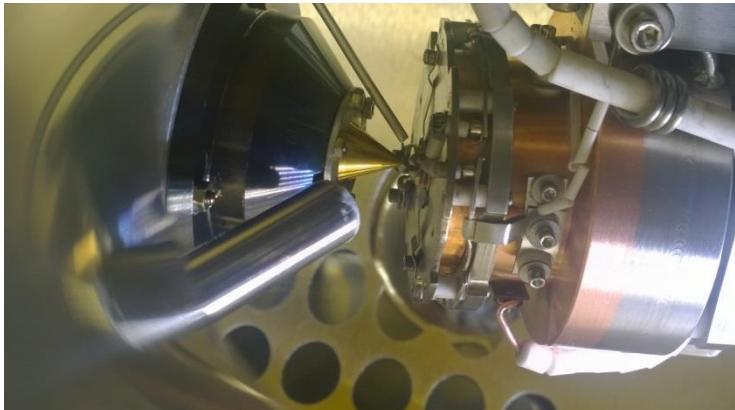


Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS) endstation at NSLS-II

AP-XPS End Station

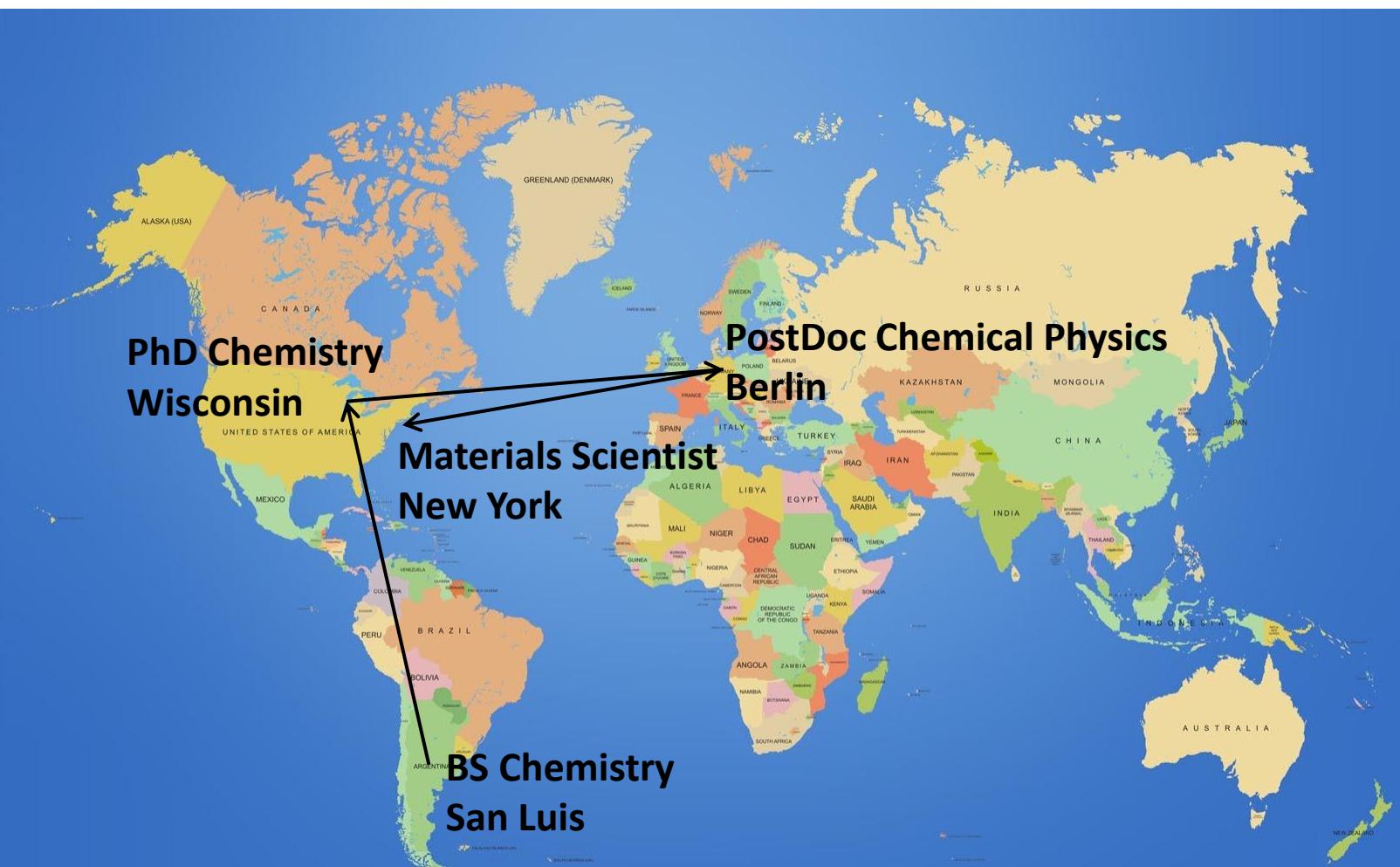


Photon Energy: 250 eV to 2000 eV
Pressures up to 5 Torr.
Temperatures up to 900 C
Capillary tube into Mass Spec.

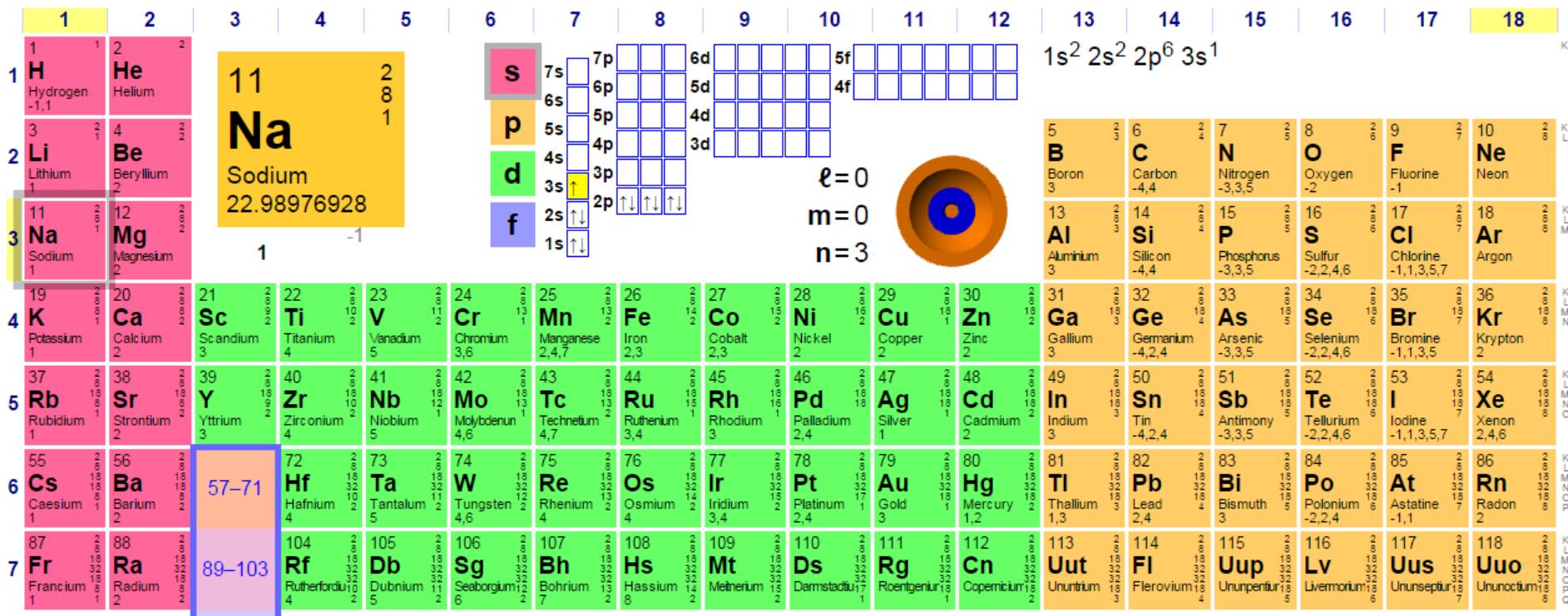


Who is this guy?

Anibal Boscoboinik - CFN, Brookhaven Lab



Our Playground



What will you learn today?

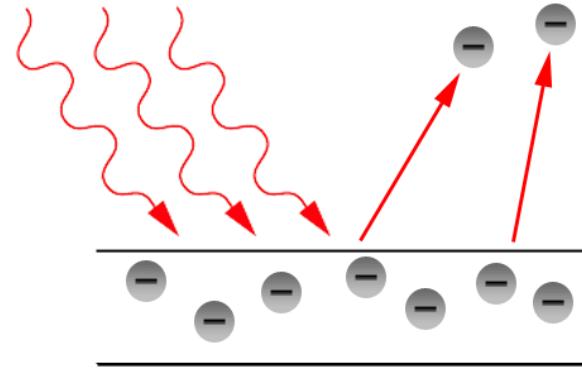
- X-ray Photoelectron Spectroscopy (XPS)
- Ambient Pressure XPS.
- What you can do with it.
- Some examples.

X-ray Photoelectron Spectroscopy

- **Background**

Photoelectric Effect

The **photoelectric effect** is the observation that many metals emit **electrons** when **light** shines upon them. (Hertz 1887)

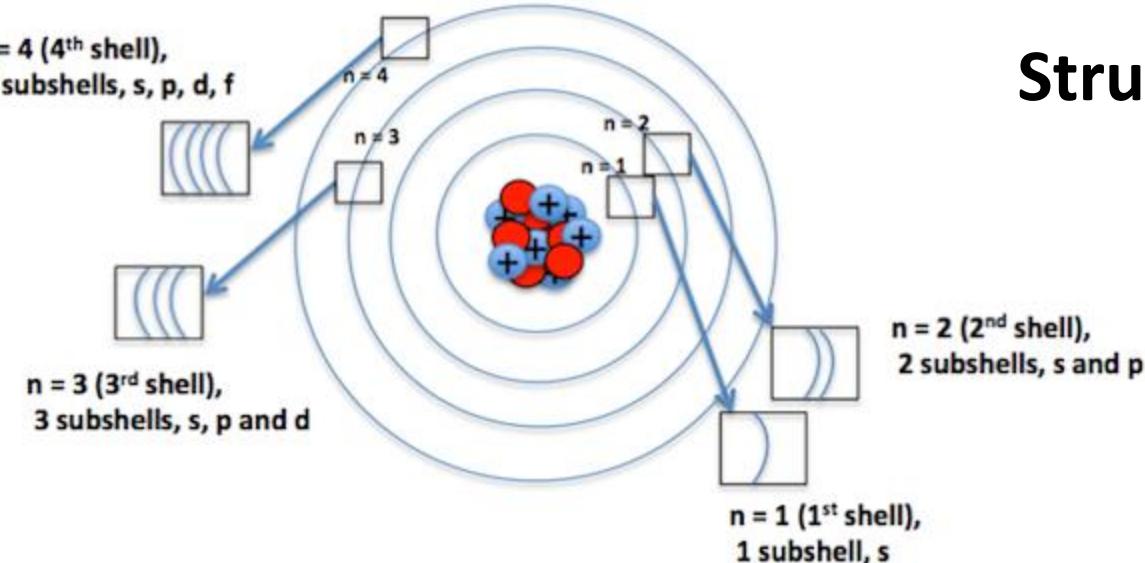


- The energy of the light must exceed certain value for emission of electrons to occur.
- The intensity of the light doesn't affect the energy of the electrons, but it affects the number of emitted electrons

In [1905 Albert Einstein](#) published a paper that explained experimental data from the photoelectric effect as being the result of light energy being carried in discrete quantized packets (**Photon**). → Nobel Prize 1921.

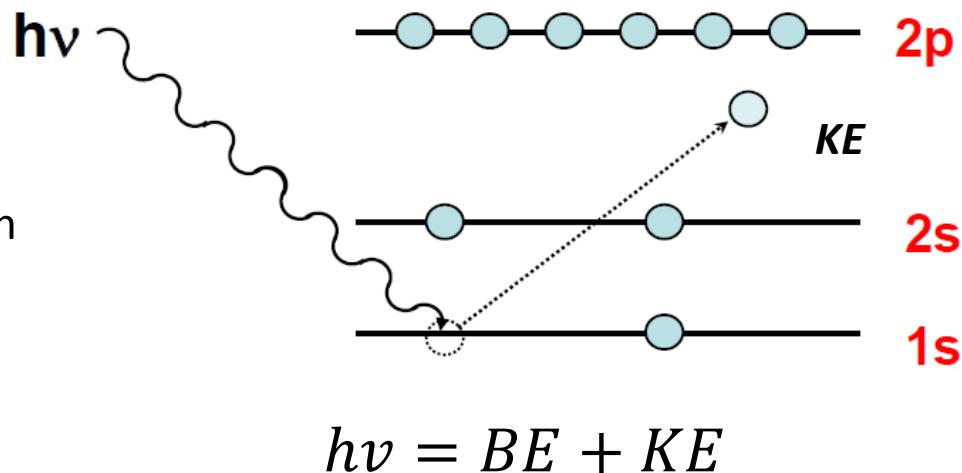
$$E = h\nu$$

Structure on an atom

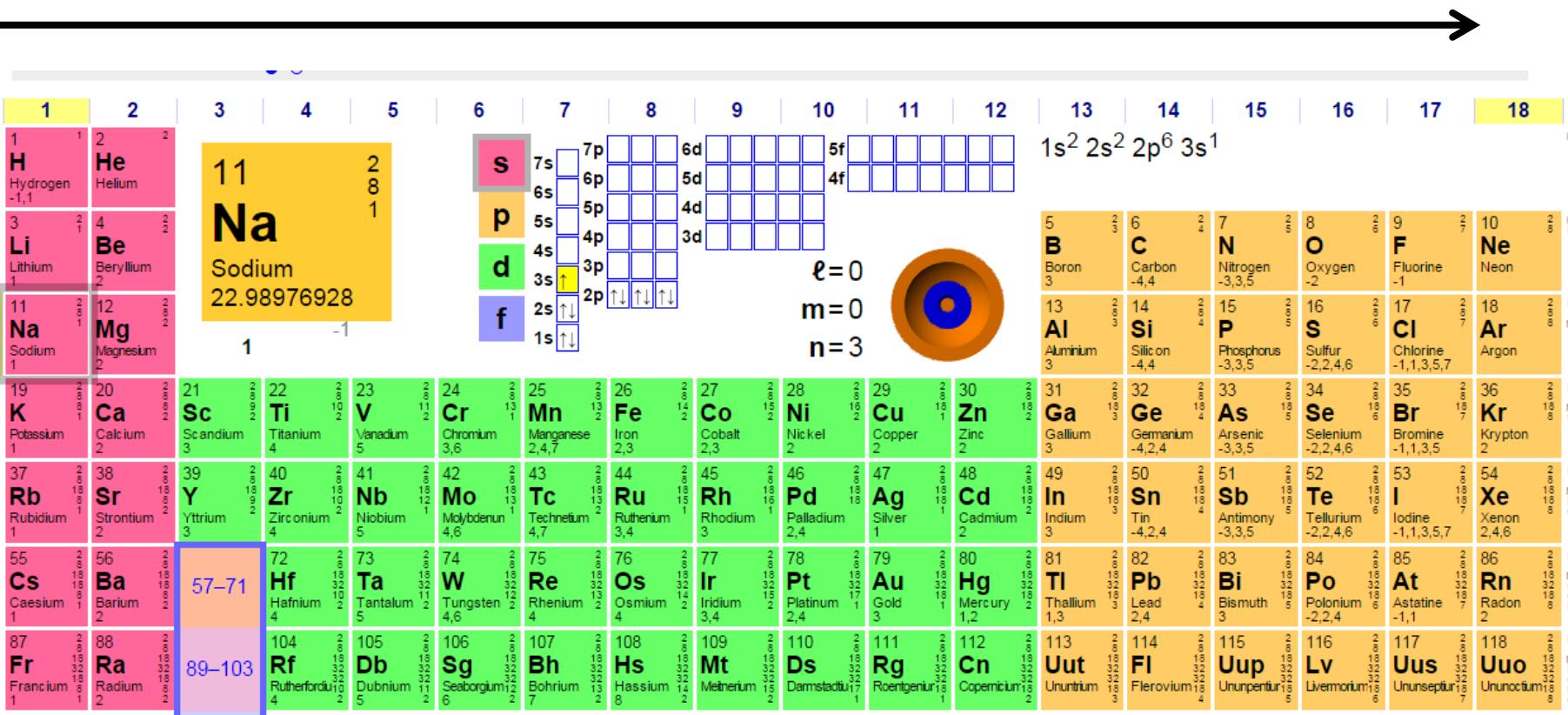


Shells and Subshells

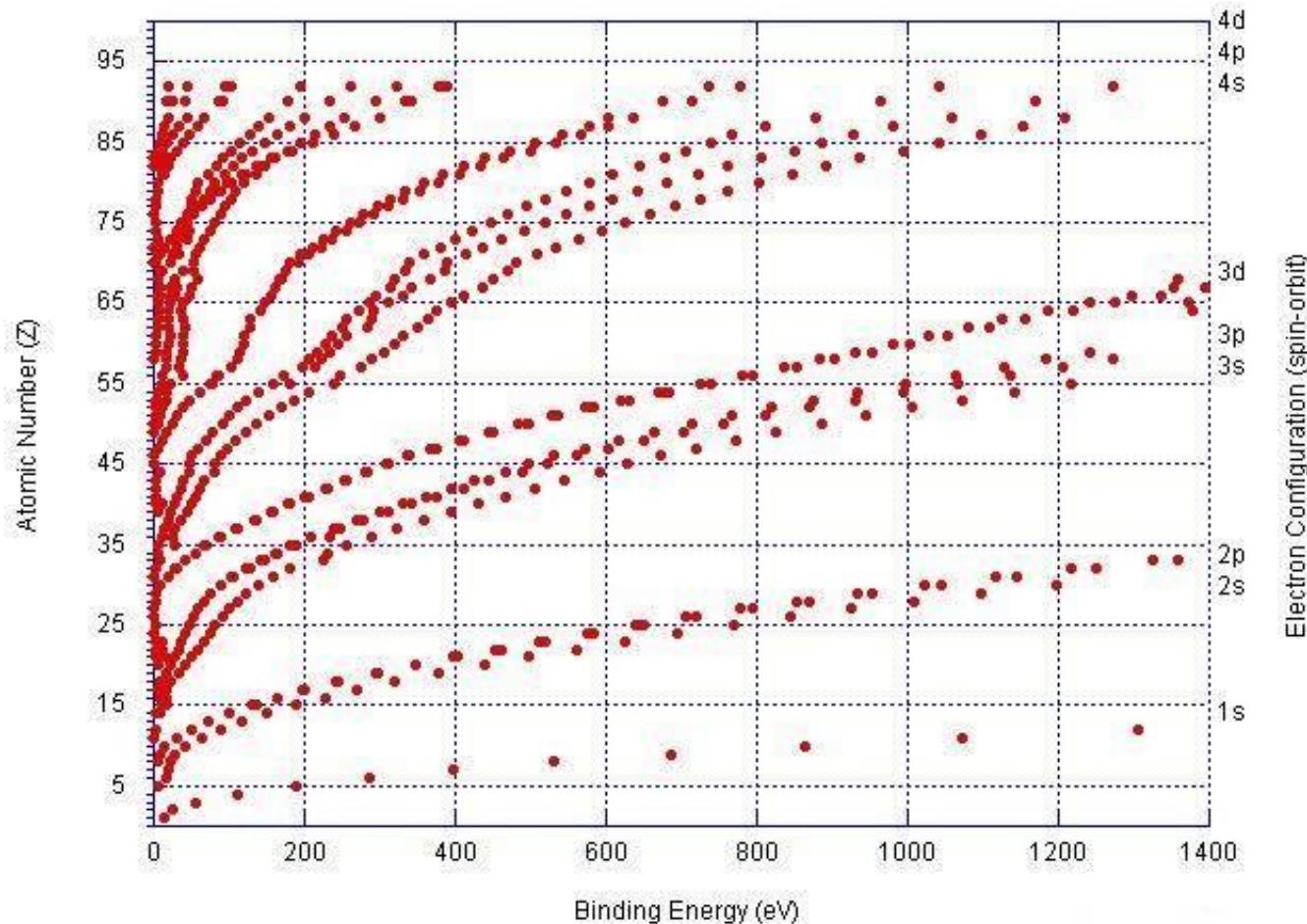
- A photon ($E=h\nu$) is absorbed by an electron
- The electron is emitted from the atom with certain KE



Periodicity Table, binding Energies



Binding Energy vs Atomic # vs Electron Configuration



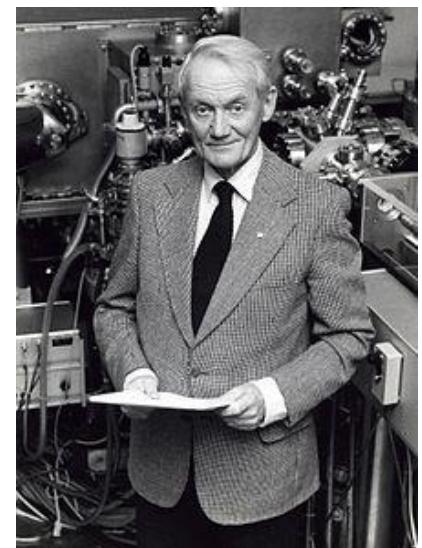
X-ray Photoelectron Spectroscopy

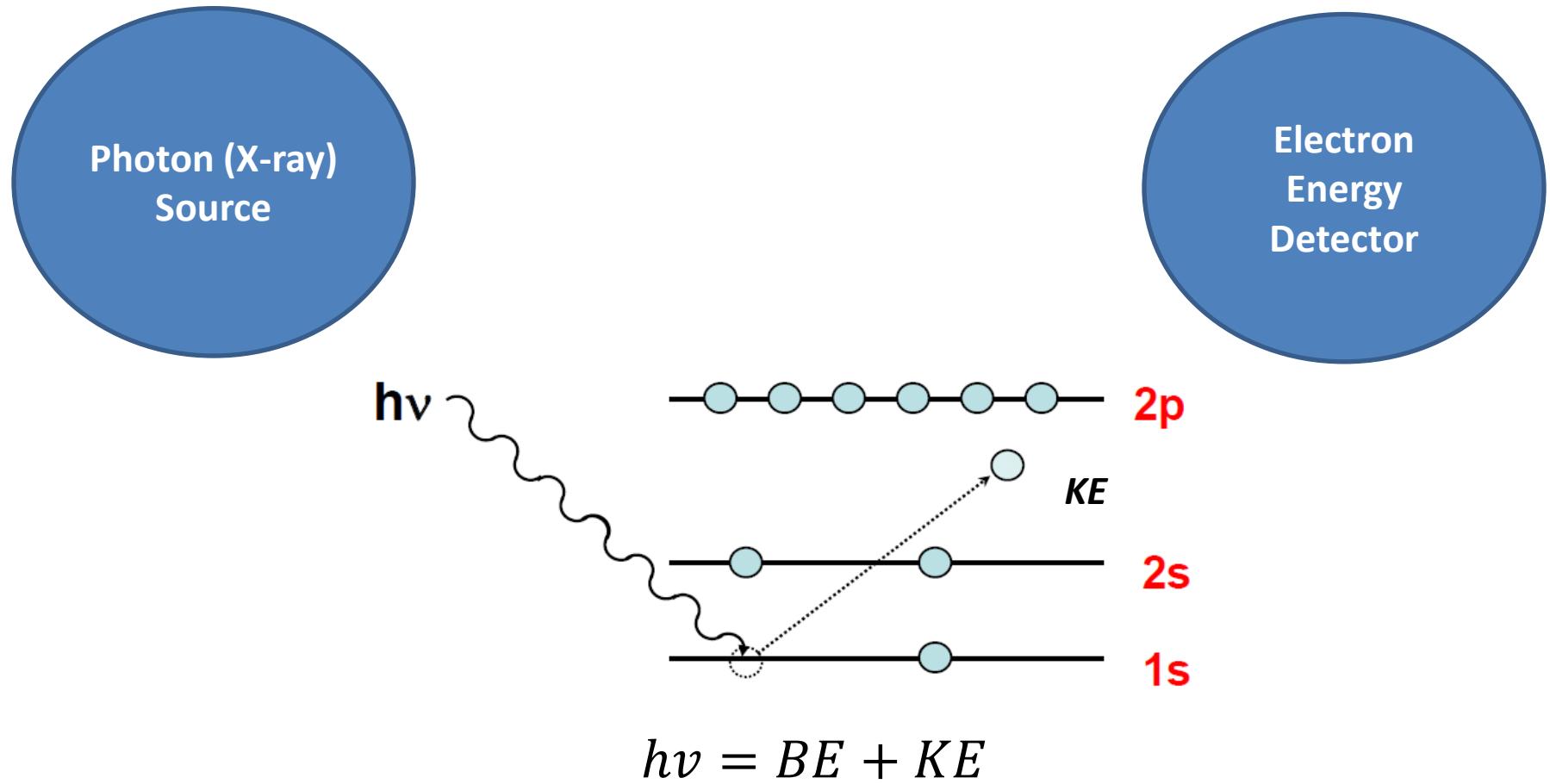
- Background
- Principles

- **Karl Manne Georg Siegbahn.**
Nobel Prize in Physics in 1924 "for his discoveries and research in the field of X-ray spectroscopy."

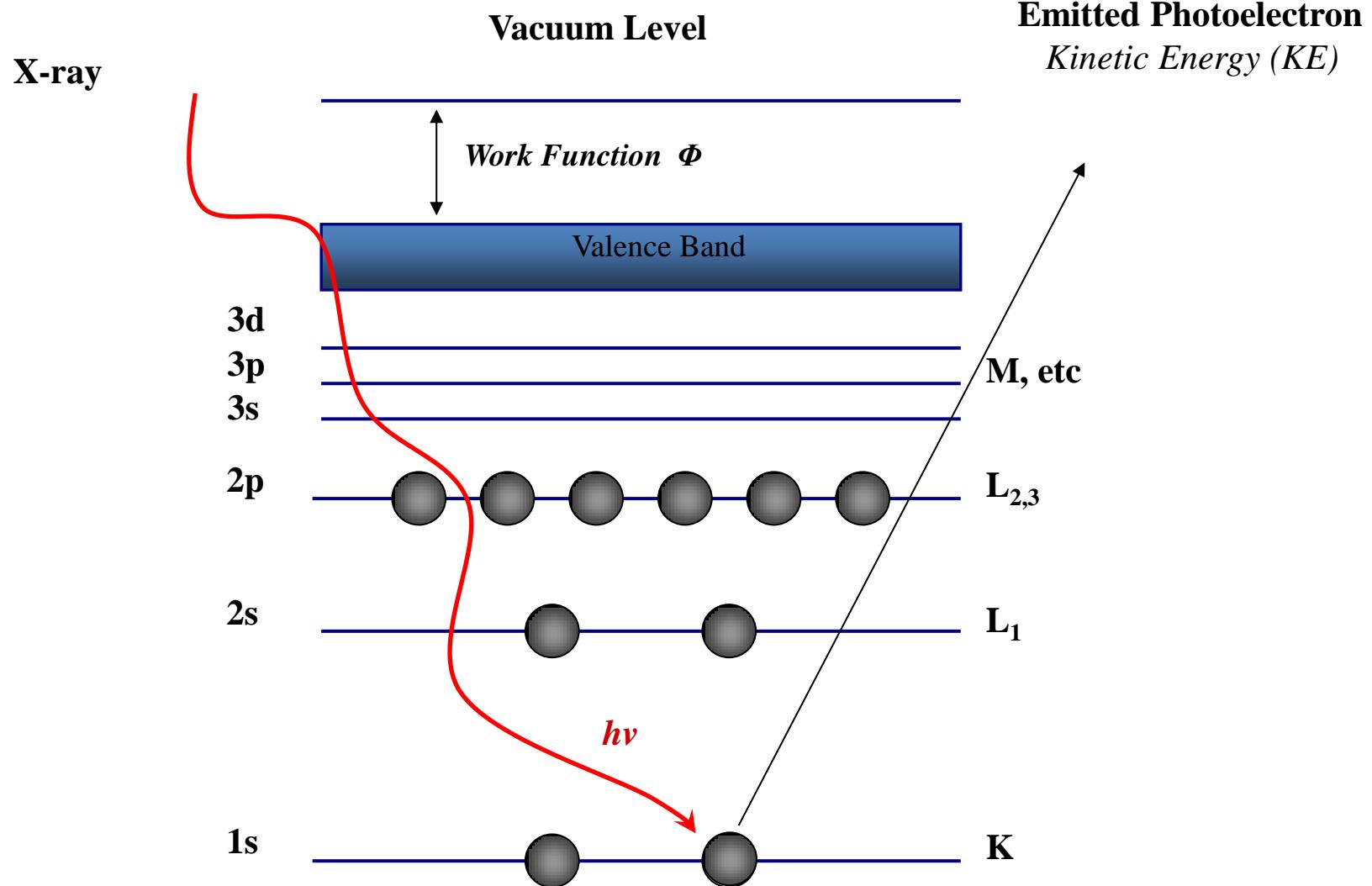


- **Kai Manne Börje Siegbahn.**
Nobel Prize in Physics in 1981 "for developing the method of **Electron Spectroscopy for Chemical Analysis** (ESCA), now usually described as X-ray photoelectron spectroscopy (XPS)"





X-ray Photoelectron Spectroscopy (XPS)

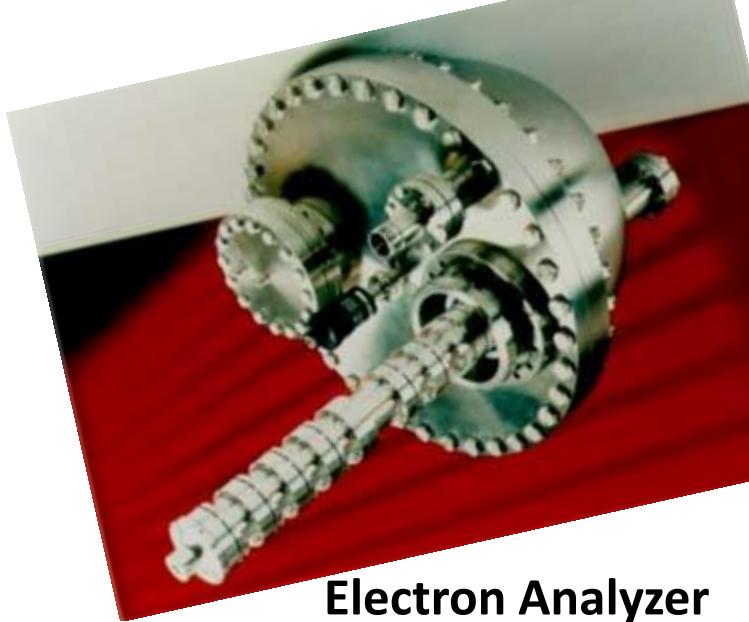


$$h\nu = BE + KE$$

Columbia University, Oct 14th 2015. Anibal
Boscoboinik - CFN, Brookhaven Lab

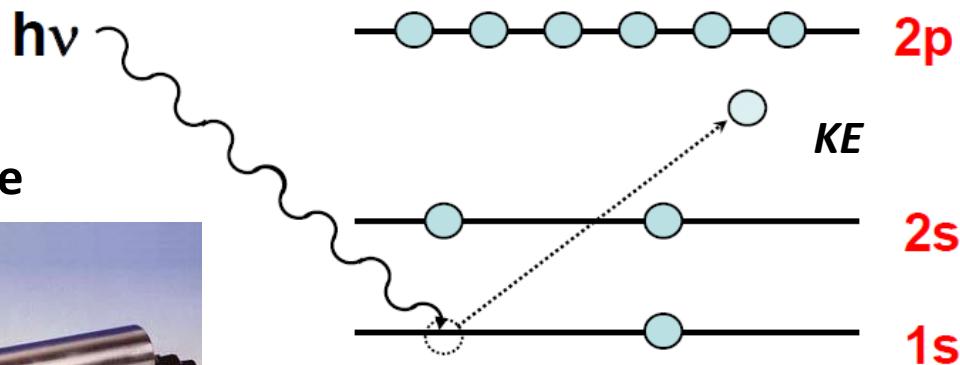
Courtesy of O. Furlong (UNSL)
14

Synchrotron



Electron Analyzer

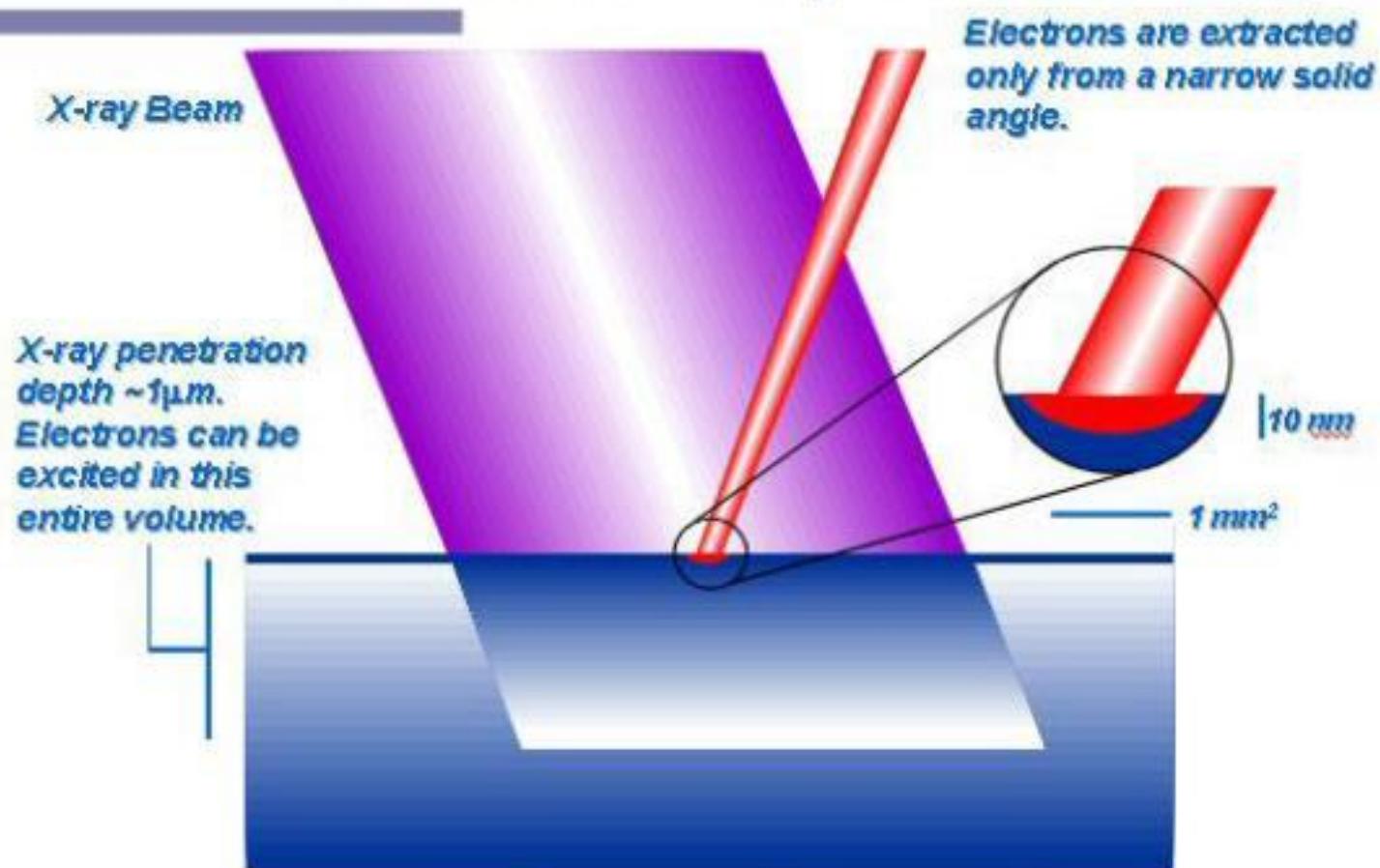
Lab X-ray source



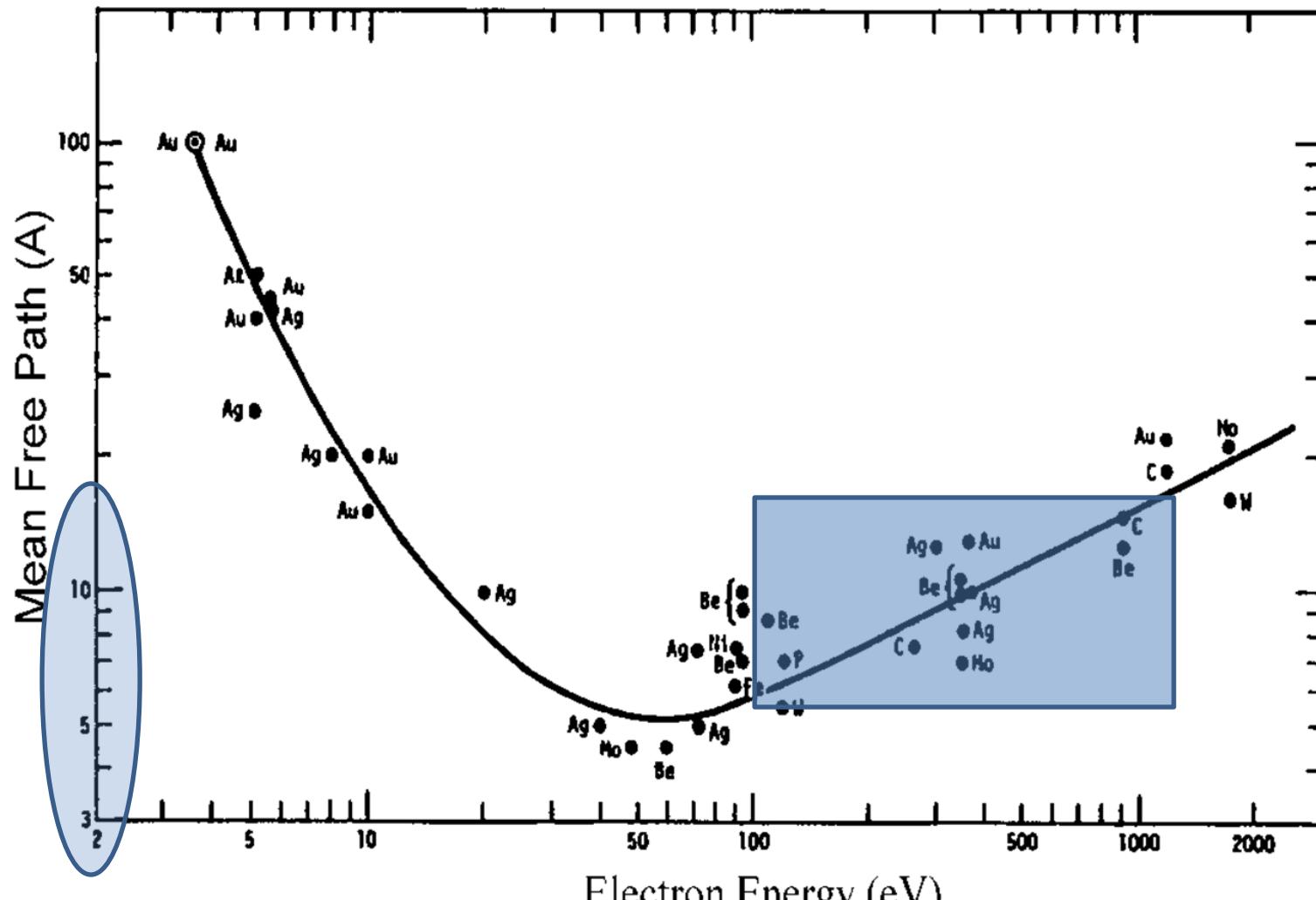
$$h\nu = BE + KE$$

Why is XPS surface sensitive?

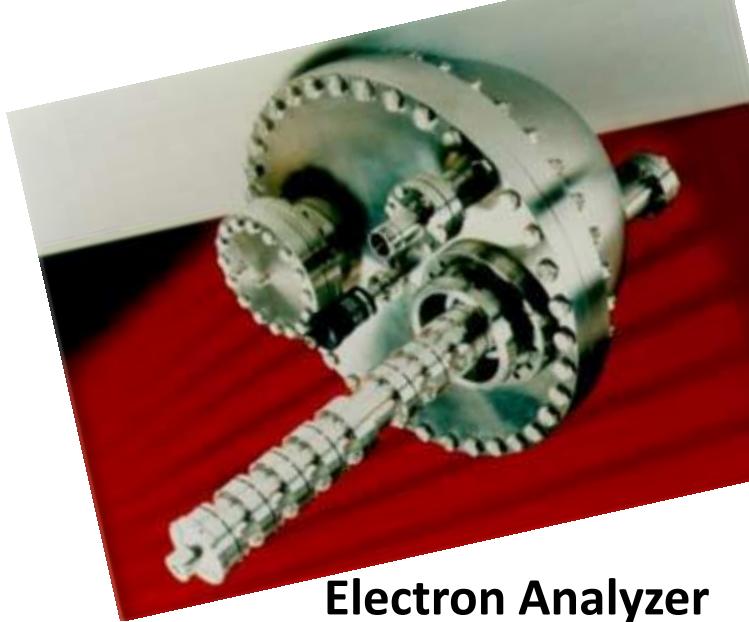
X-ray Photoelectron Spectroscopy



Electron Escape Depth



Synchrotron



Electron Analyzer

Lab X-ray source



$h\nu$



$2p$

KE

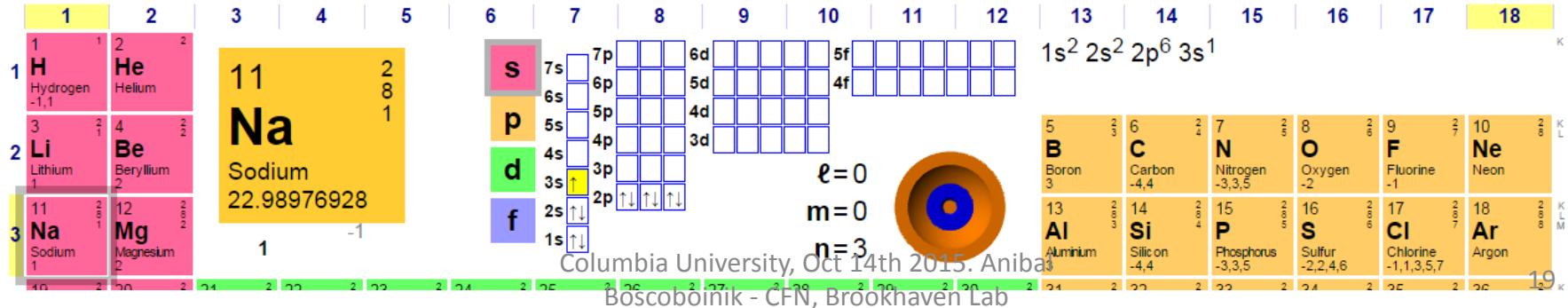
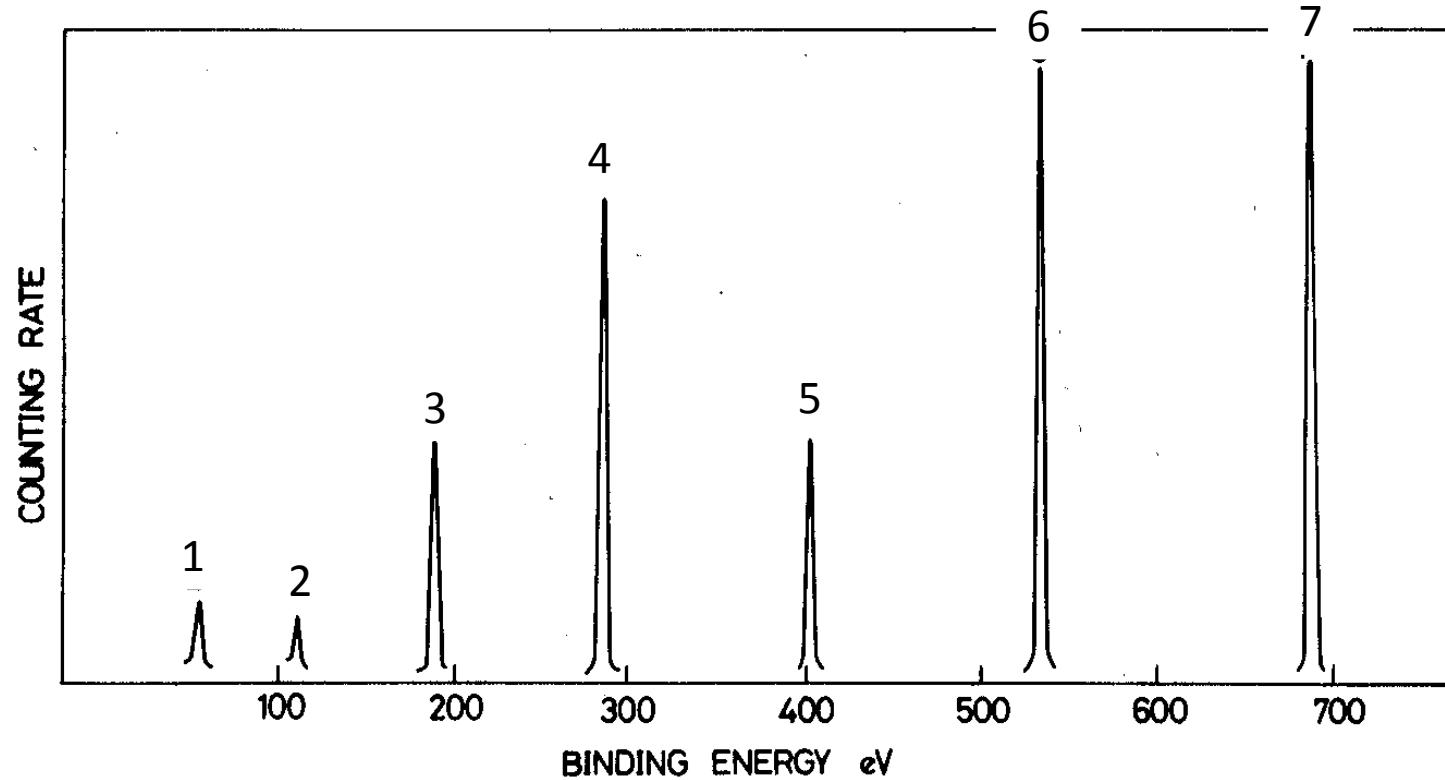


$2s$

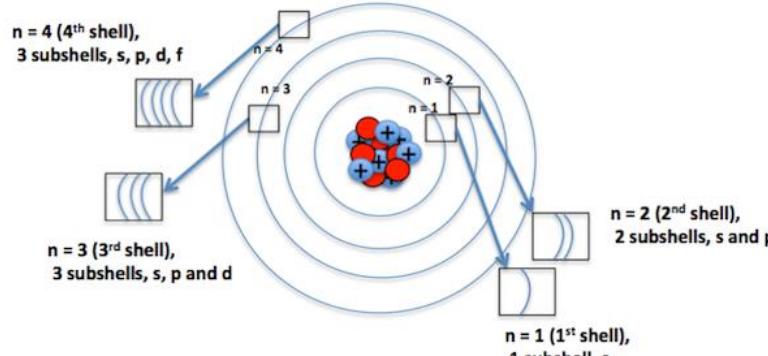
$1s$

$$h\nu = BE + KE$$

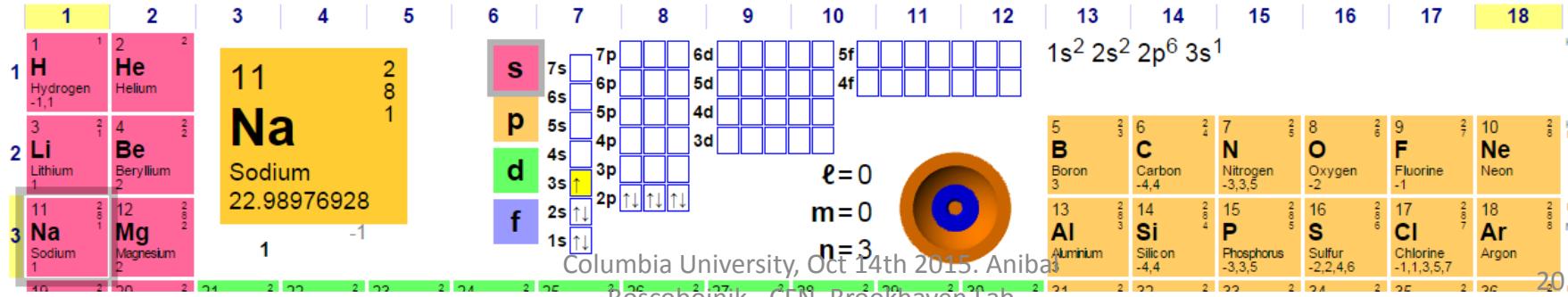
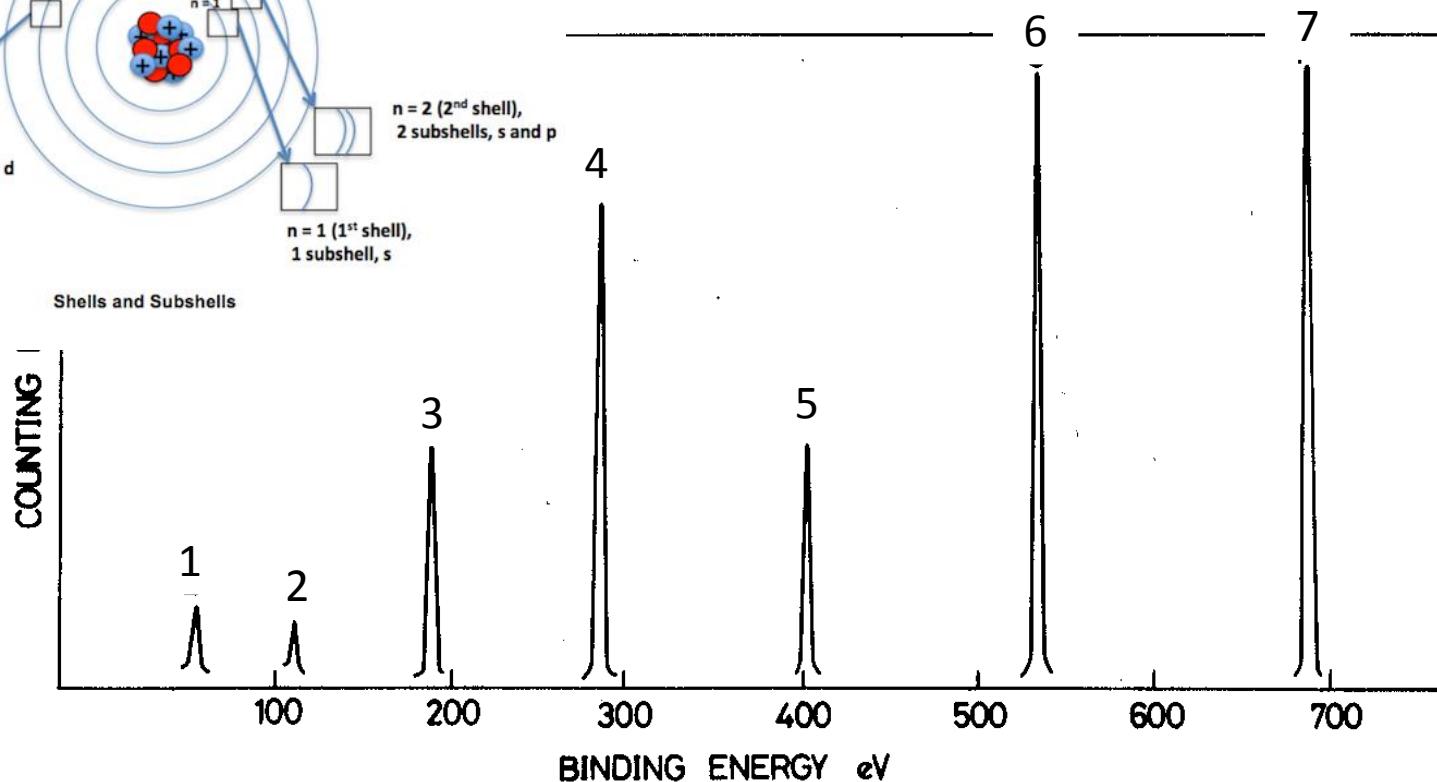
1s binding energies for these elements: B, C, O, Be, F, Li, N



These elements: B, C, O, Be, F, Li, N



Shells and Subshells

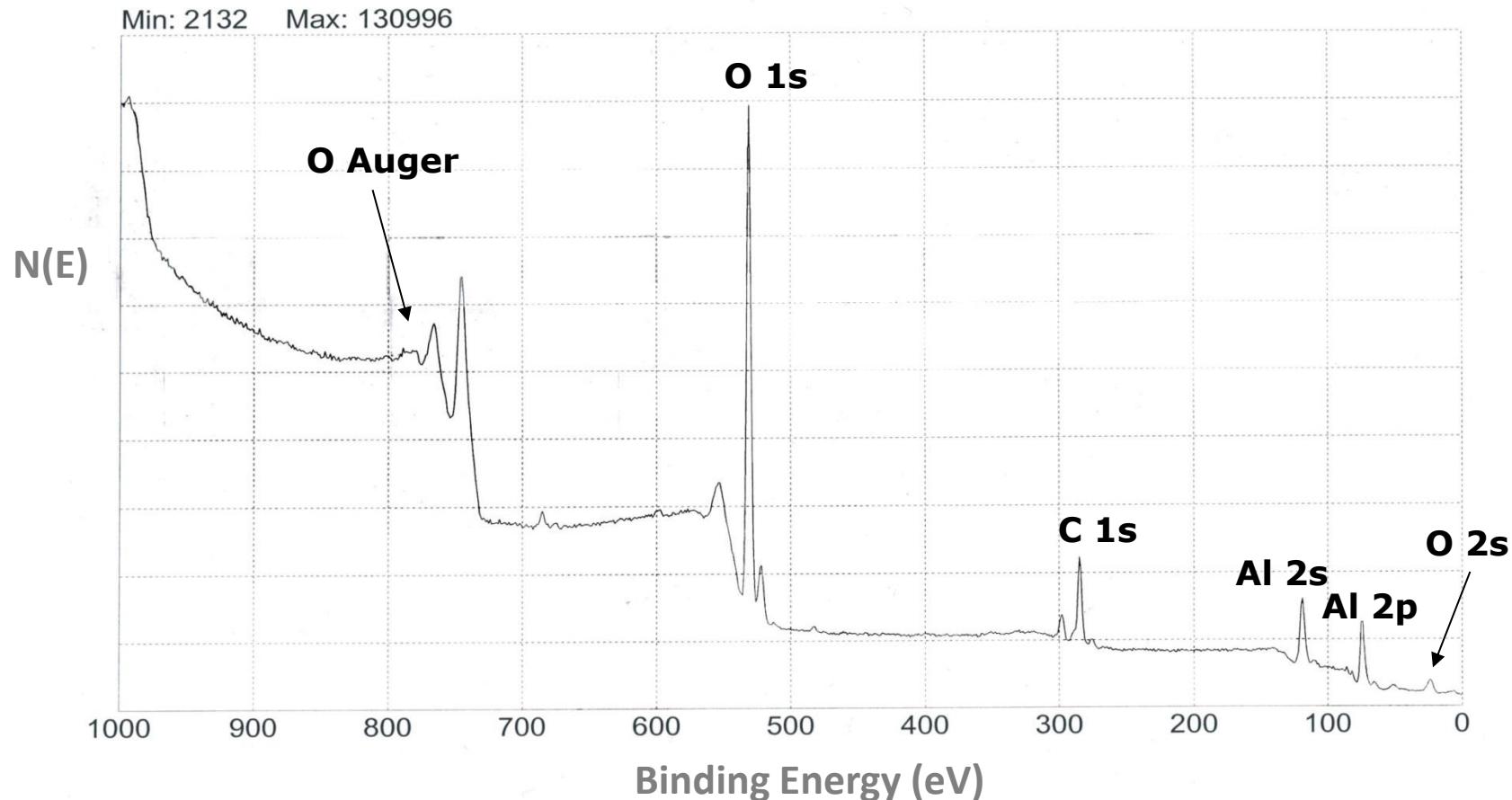


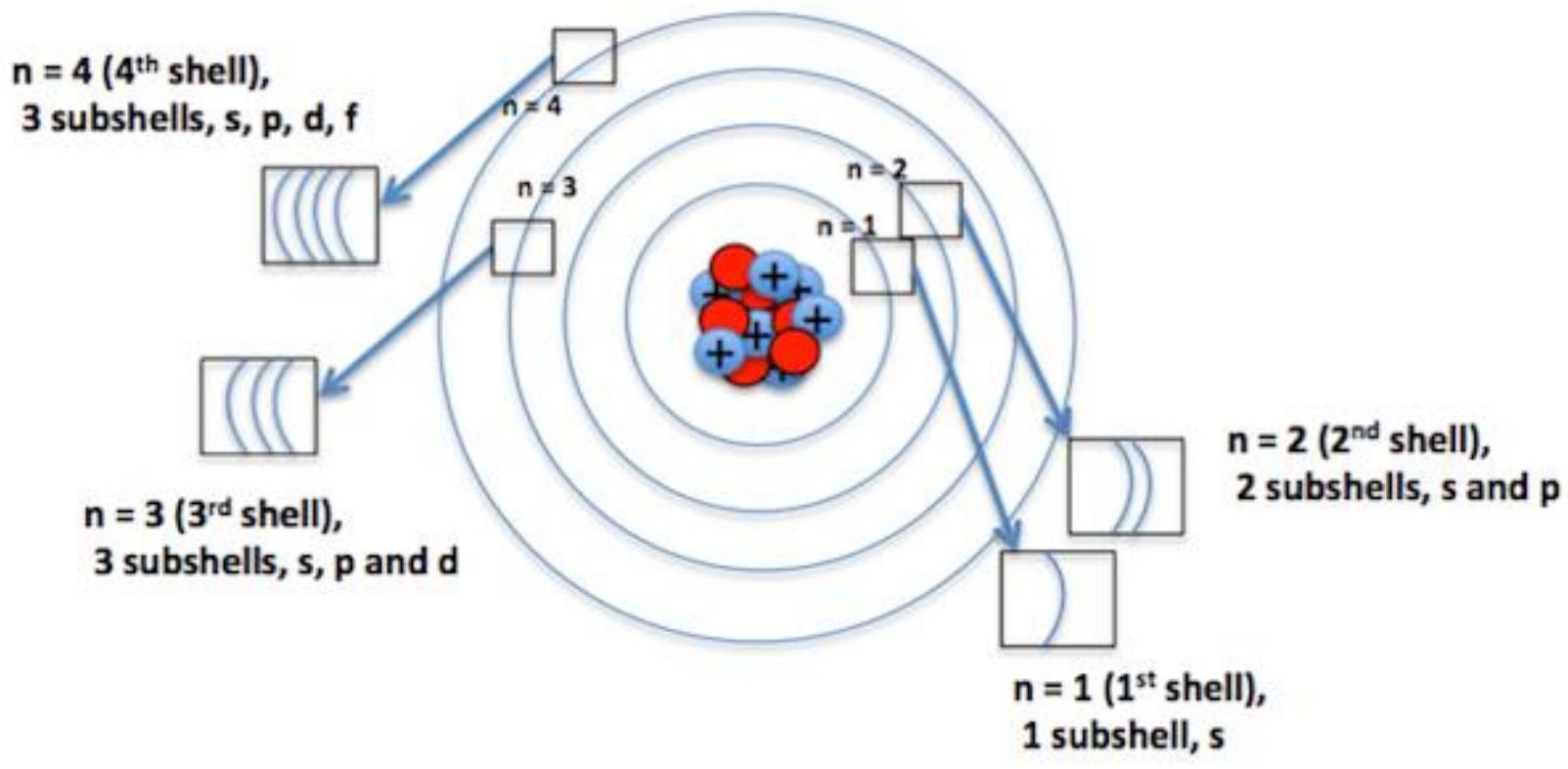
Aluminum Plate

XPS Survey

EV/Step: 1 eV, Time/Step: 50 mSec, Sweeps: 10

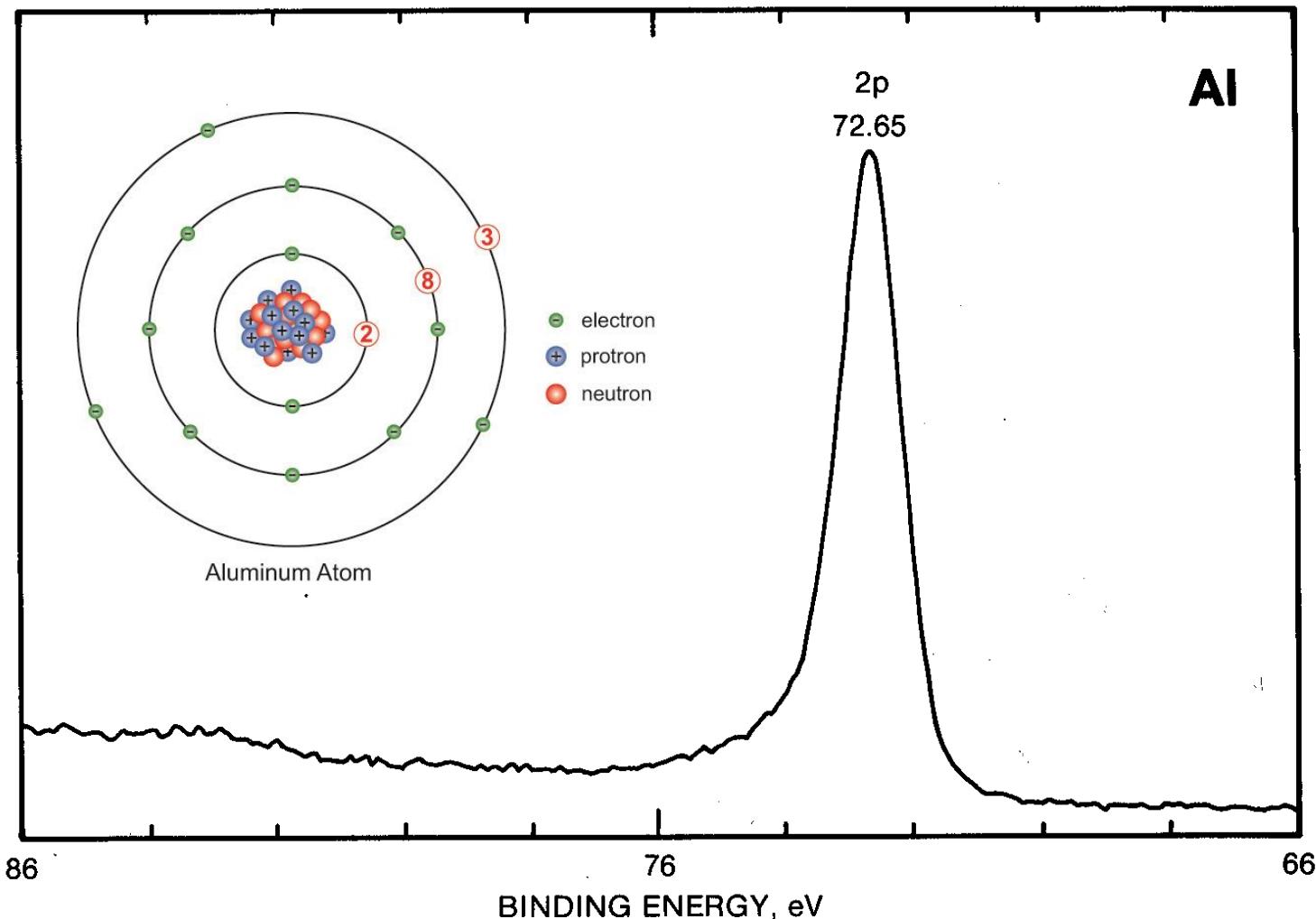
Source: Mg $K\alpha$, Pass Energy: 100 eV



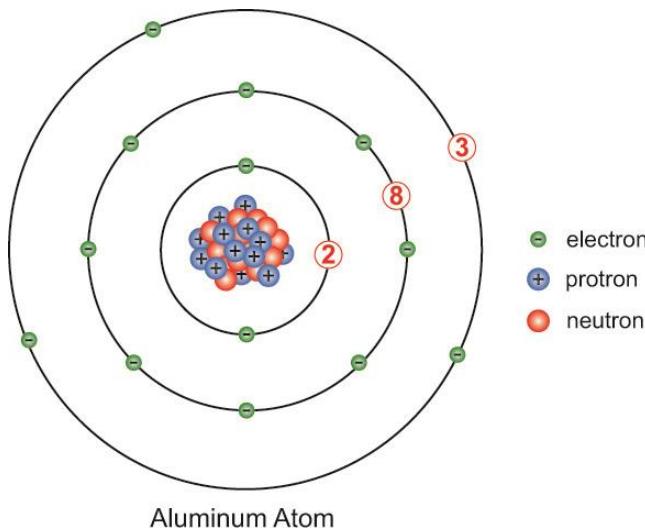


Shells and Subshells

Metallic Aluminum

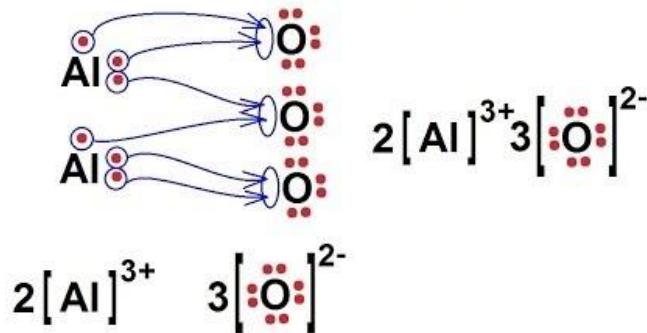


Metallic Aluminum

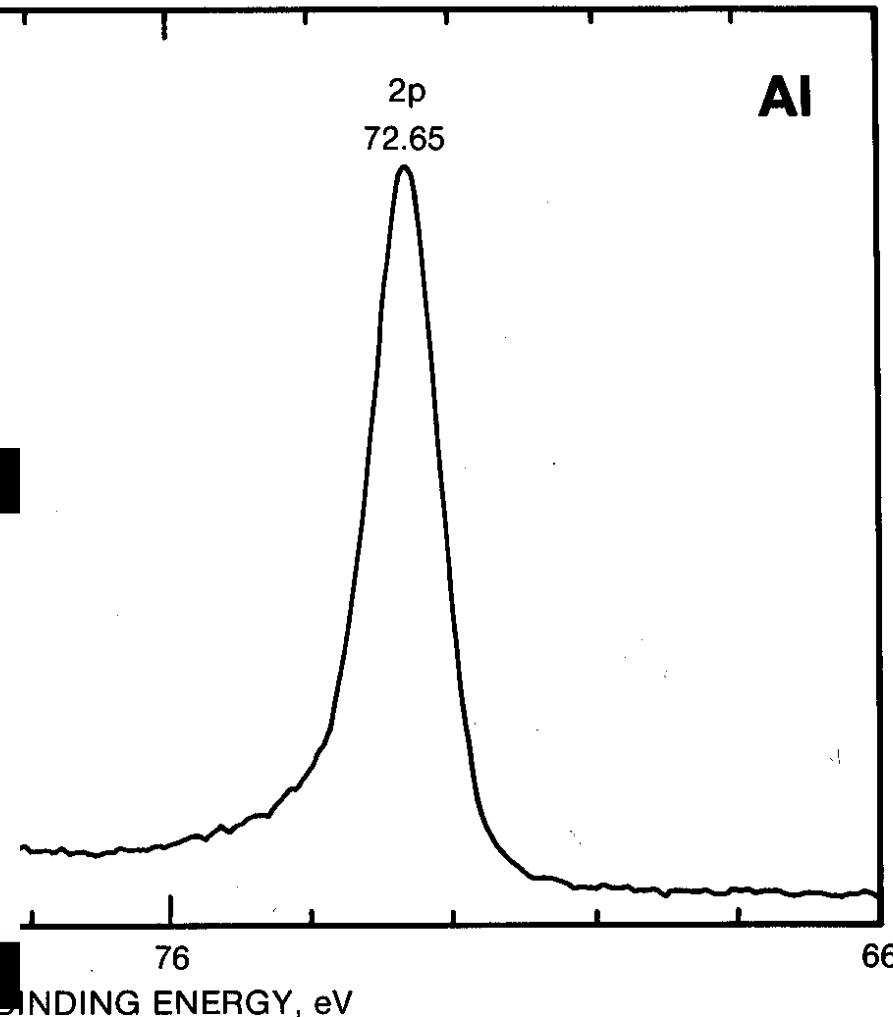


Aluminum Oxide Al_2O_3

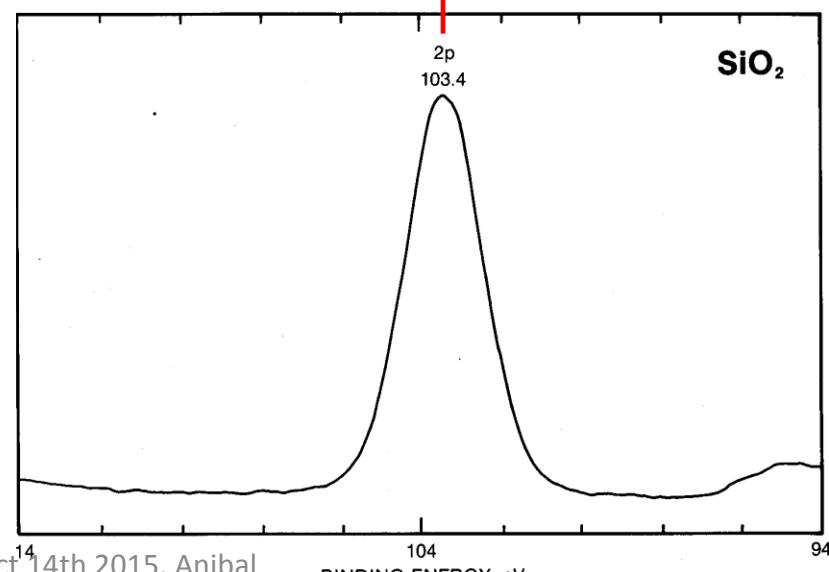
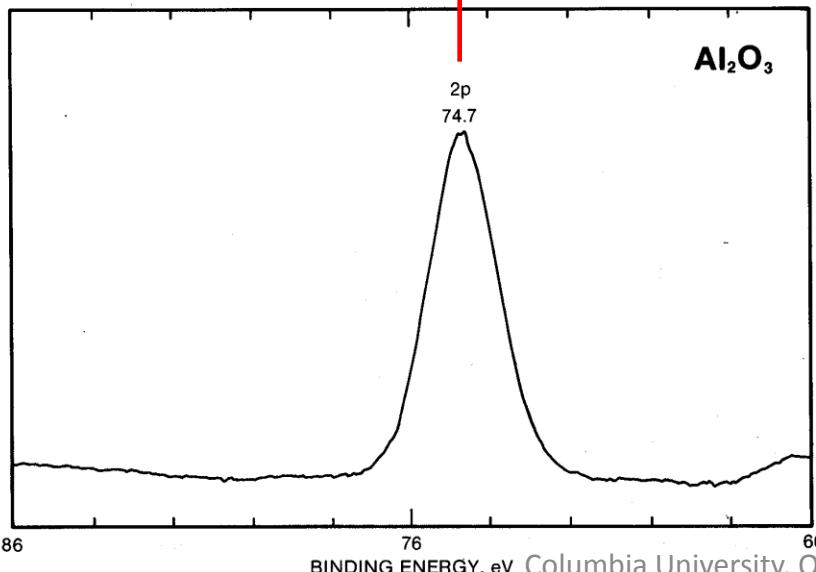
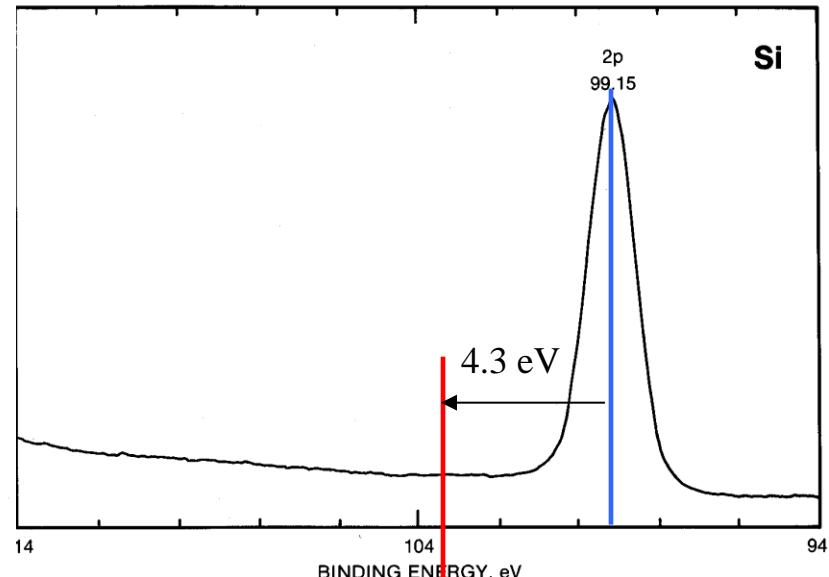
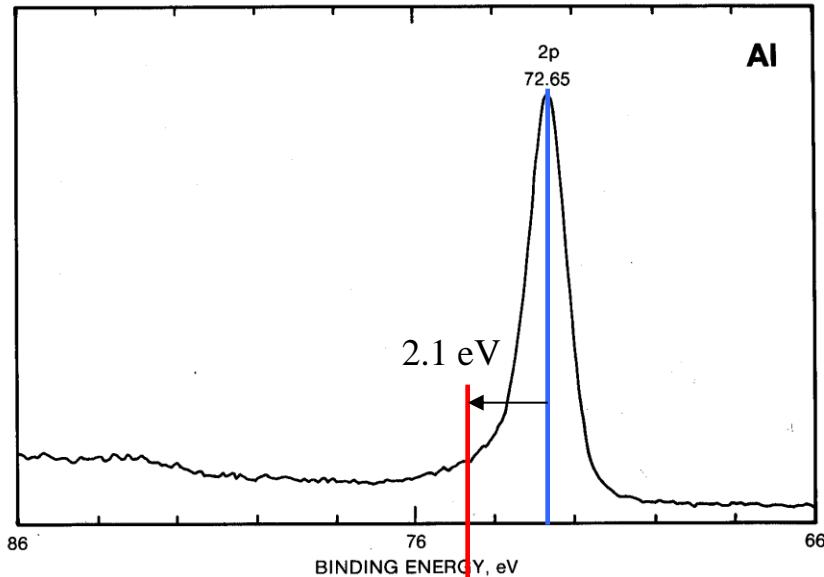
$\text{Al} \rightarrow$ donates $3 \times 2 = 6e^-$
 $\text{O} \rightarrow$ needs $2 \times 3 = 6e^-$

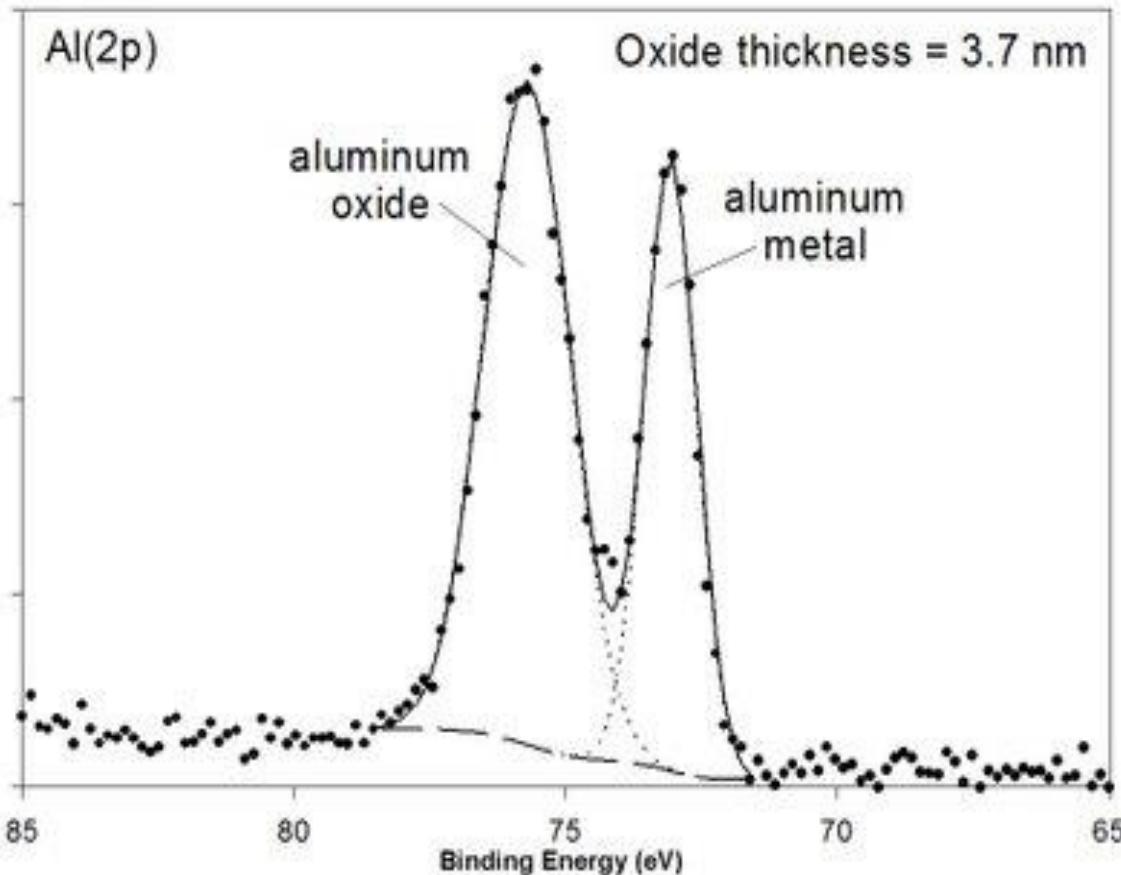


What happens if we oxidize it?

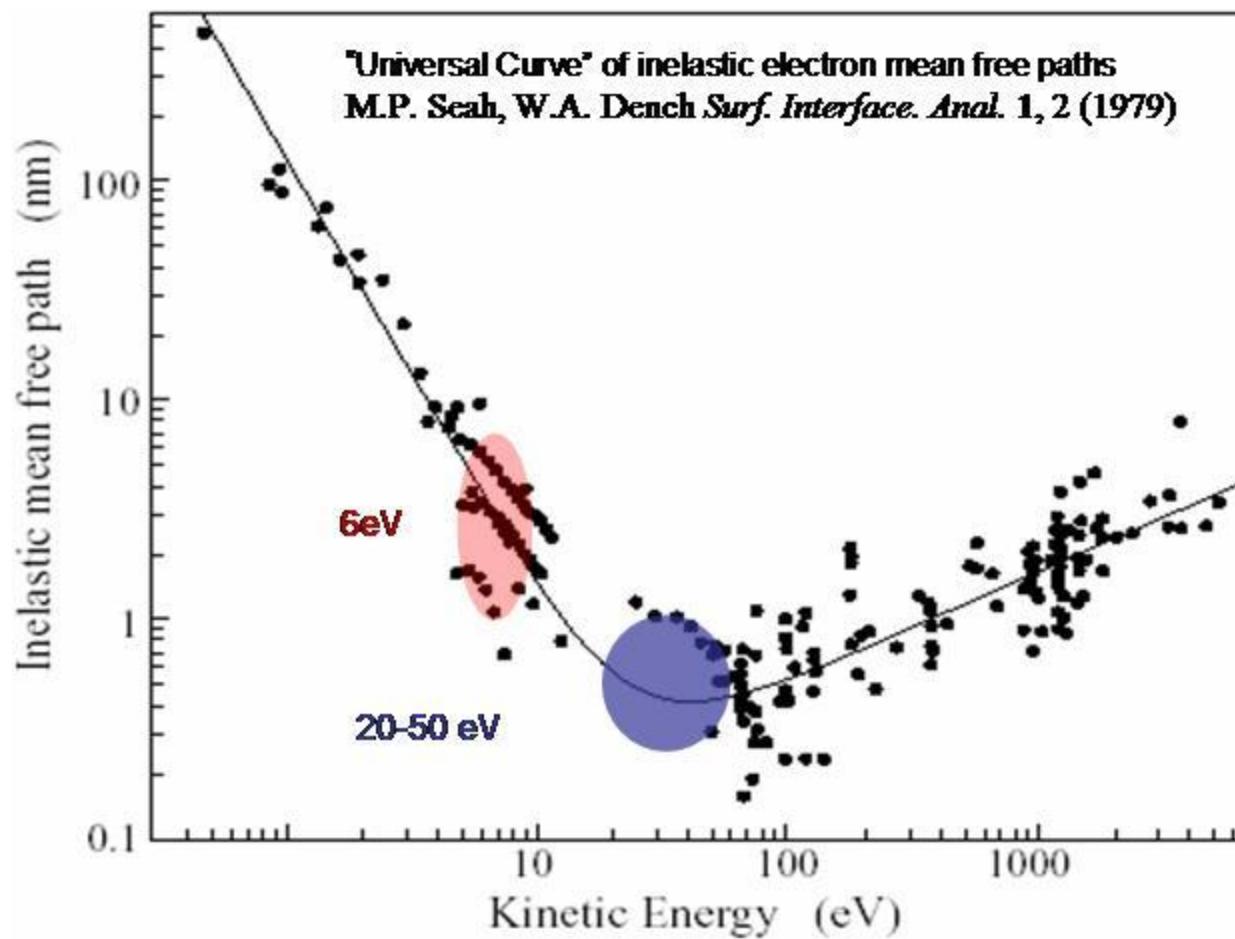


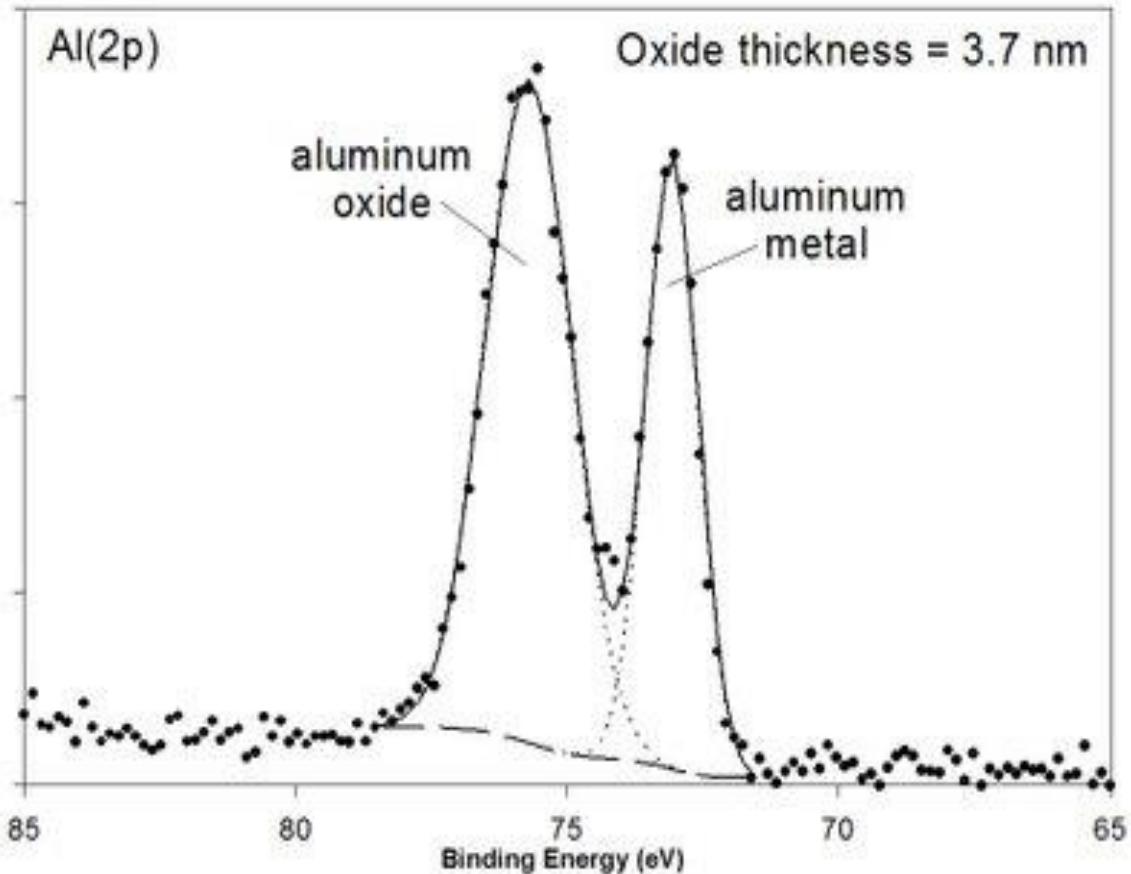
Oxidation State





How can you determine the oxide thickness?



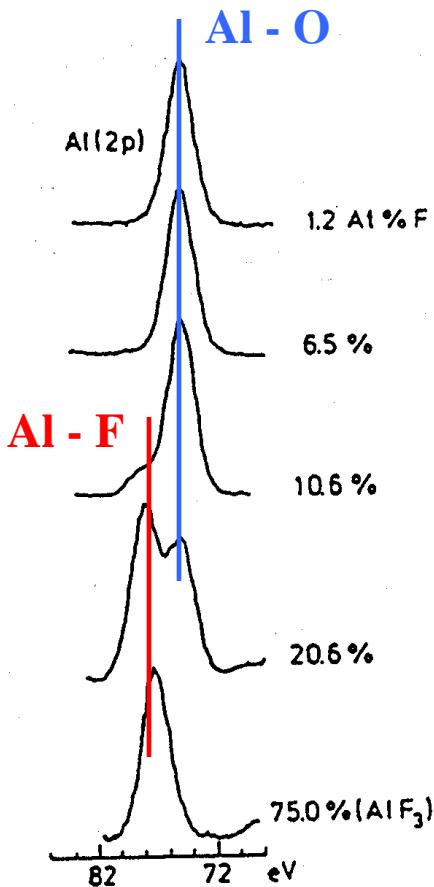


Al - O



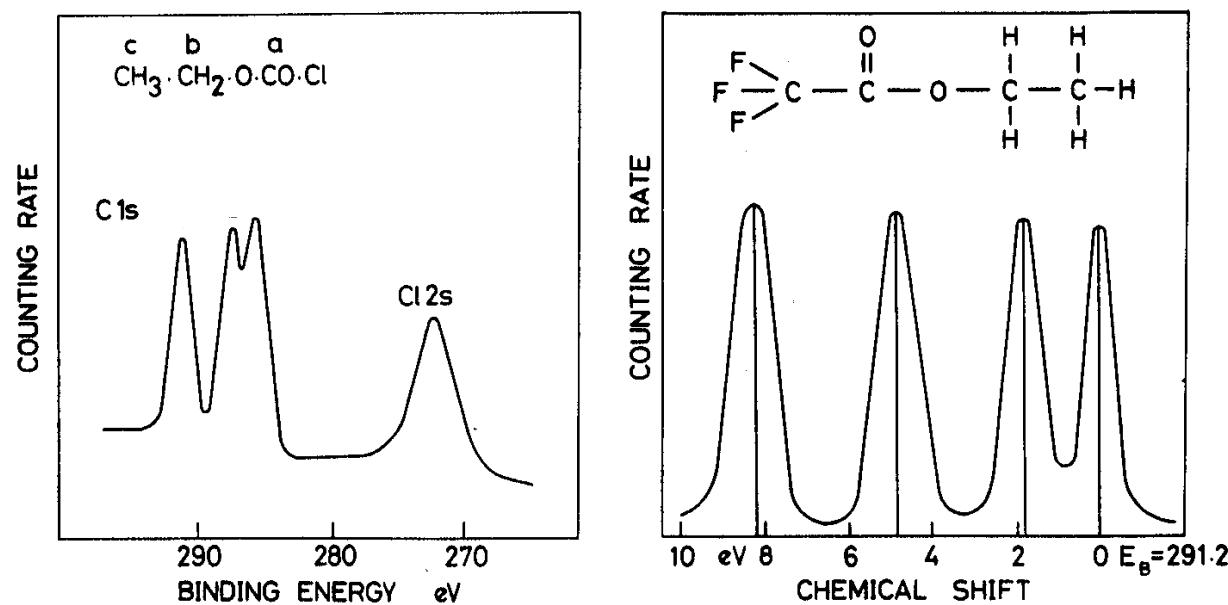
Al - F

Chemical Shift



1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H Hydrogen 2.20	2 He Helium 2 K	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 Li Lithium 0.98	2 Be Beryllium 1.57	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 Mn Manganese 54.938044	2 B Boron 2.04	3 C Carbon 2.55	4 N Nitrogen 3.04	5 O Oxygen 3.44	6 F Fluorine 3.98	7	8	9	10	11	12	13	14	15	16	17	18

- Series..... Transition
- State at 0 K..... Solid
- Melting Point..... 1519 K
- Boiling Point..... 2334 K
- Electronegativity..... 1.55
- Radius..... 161 pm
- Hardness..... 196 MPa
- Modulus..... 120 GPa
- Density..... 7470 kg/m³
- Conductivity..... 7.8 W/mK
- Heat..... 479 J/kgK



XPS tells you

- What elements you have
- How much you have of each of them
- Their oxidation state
- Their coordination to other elements
- How deep they are from the surface

Some fact about XPS

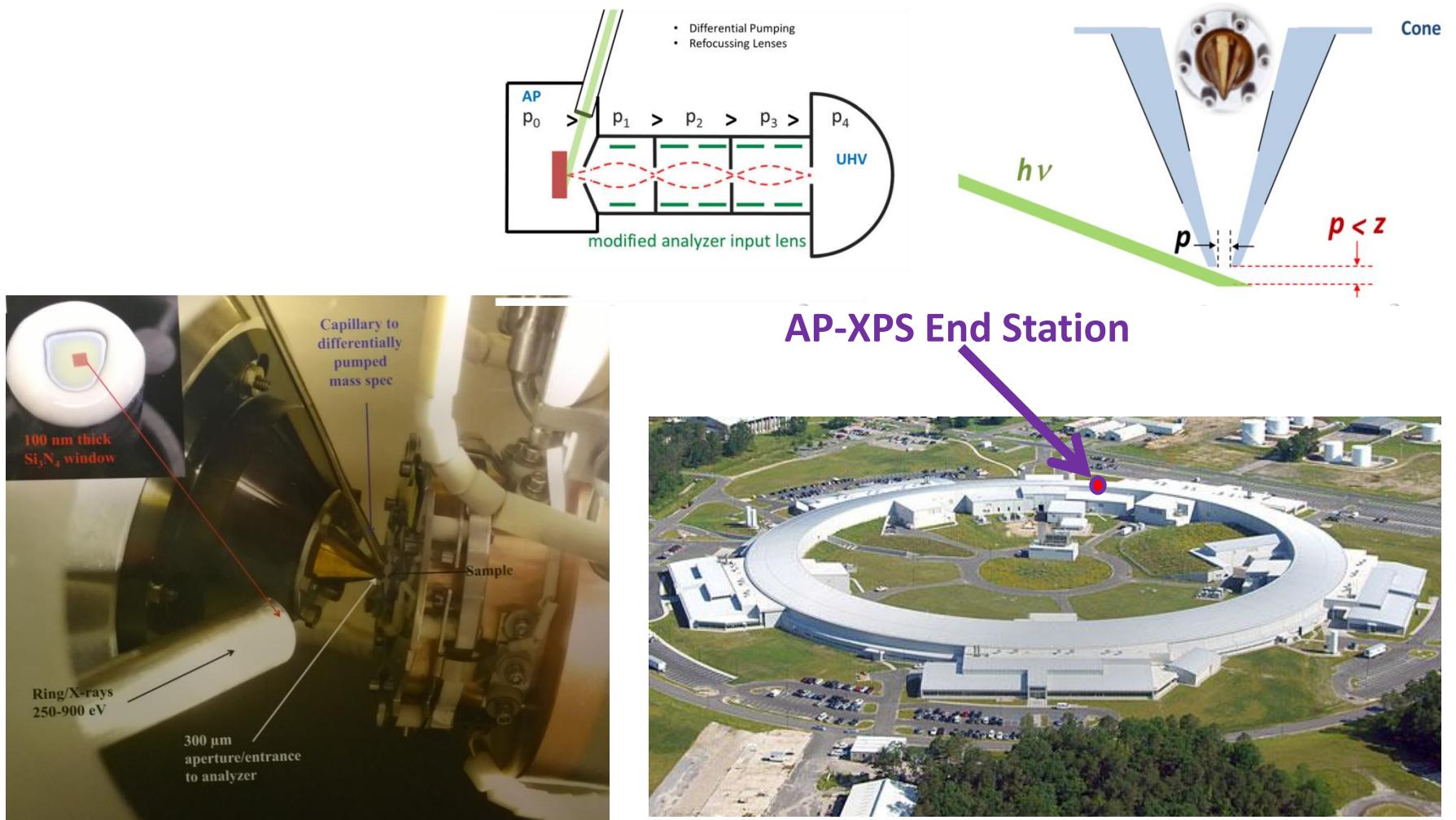
- Surface sensitive
- Traditionally carried out in UHV
- Many relevant systems require higher pressures.
 - **Catalysis**
 - Environmental and Atmospheric Chemistry

Ambient Pressure XPS

Elevated Pressures

- Developing tools at BNL
 - 1. **Ambient Pressure Photoelectron Spectroscopy (AP-PES)**
 - AP-XPS & AP-NEXAFS
 - 2. Polarization-Modulation Infrared Reflection Absorption Spectroscopy (PM-IRAS)
 - 3. Reactor-Scanning Tunneling Microscopy (r-STM)

Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS) endstation at NSLS-II

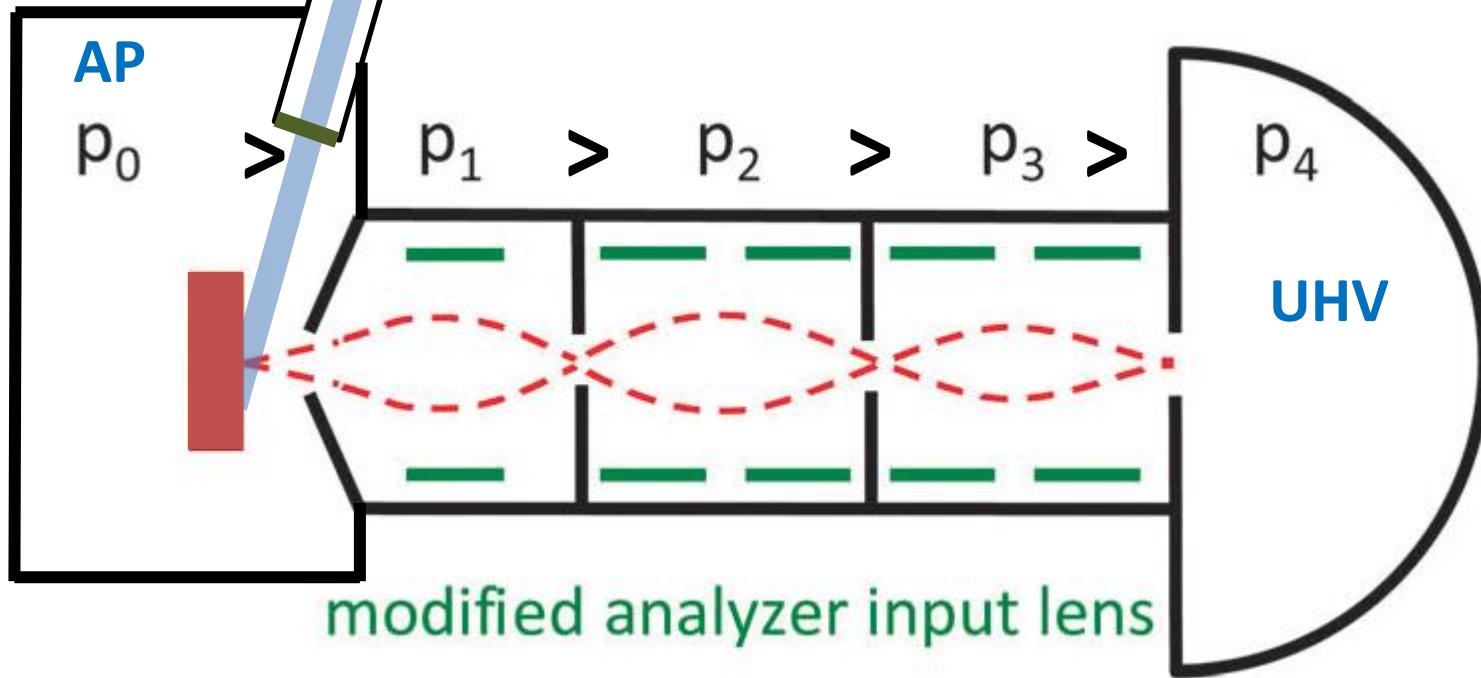


Starr, Tenney, Boscoboinik

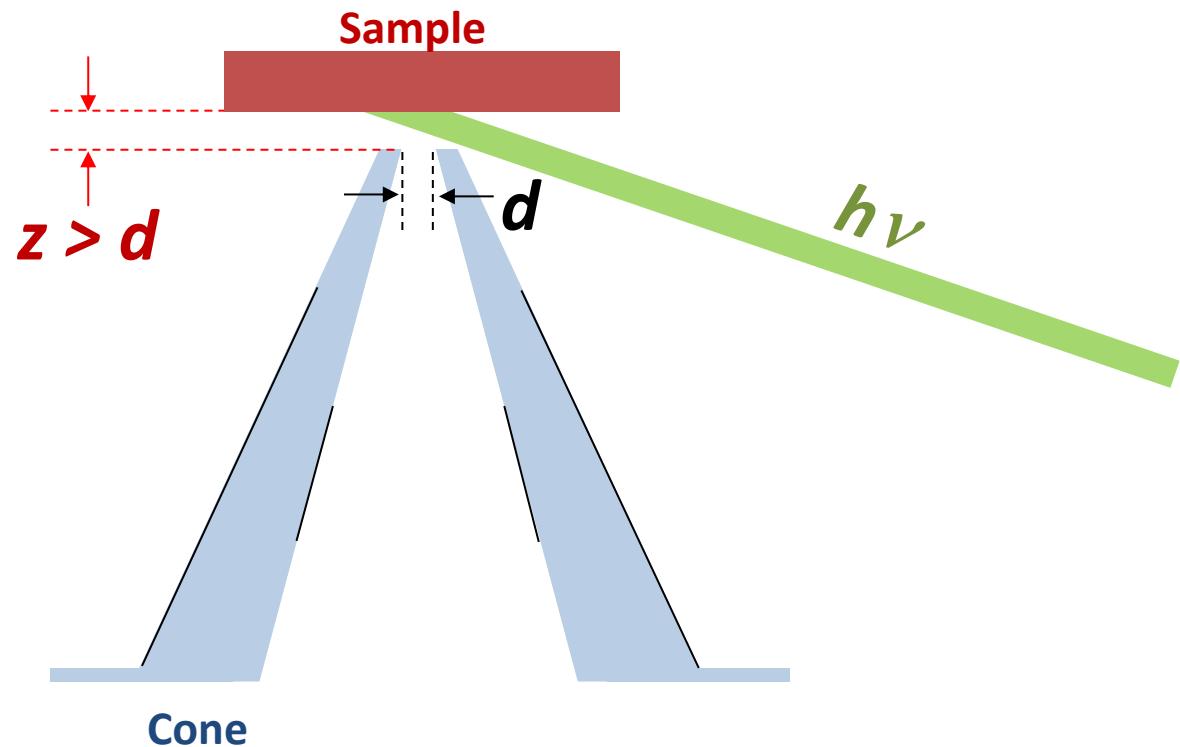
Pressures up to 5 Torr.
Capillary tube into Mass Spec.

AP-XPS

- Differential Pumping
- Refocussing Lenses



Importance of a tightly focused beam



The smaller z , the higher P_0

What can we use this for?

Catalyst Model System

Simplified version of a commercial catalyst

- allows to disentangle different factors that can potentially affect the chemical reaction.
- used for surface science mechanistic studies

There is a vast set of surface science tools to study model systems:

- Scanning Tunneling Microscopy
- X-ray Photoelectron Spectroscopy
- Etc.

'Materials Gap': Model Systems

Complexity

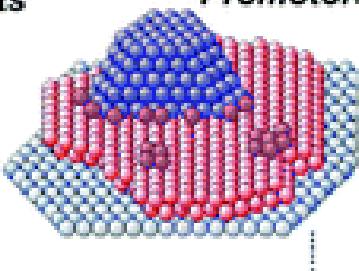
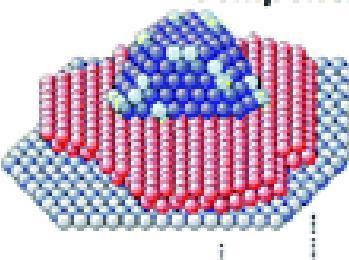
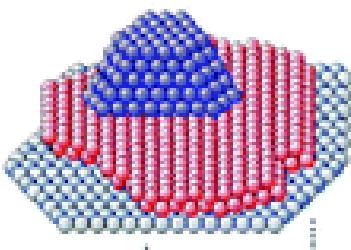
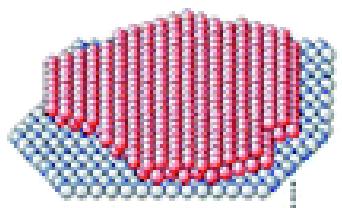
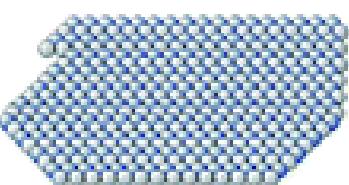
Metal Single Crystals

Oxides / Oxide Films

Metals/Oxides
Mixed Oxides

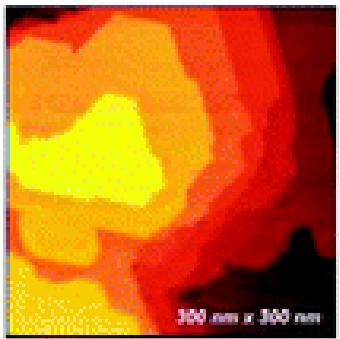
Multiple Components

Poisons
Promotors

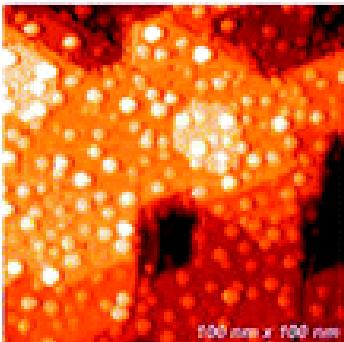


$Pd(111)$

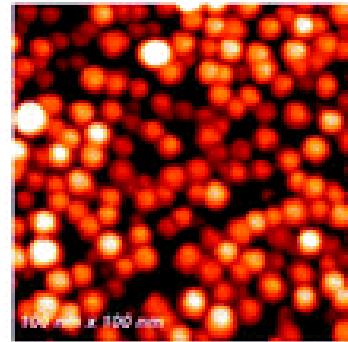
$Fe_3O_4/Pt(111)$



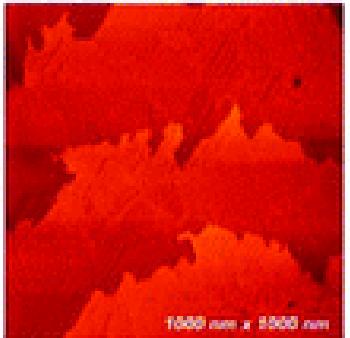
$Pd/Fe_3O_4/Pt(111)$



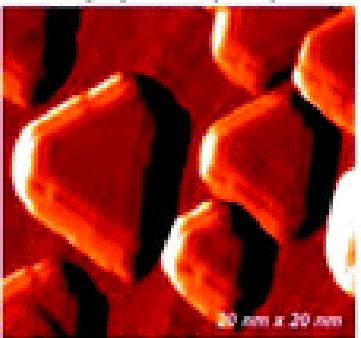
$Pd,PdO/Fe_3O_4/Pt(111)$



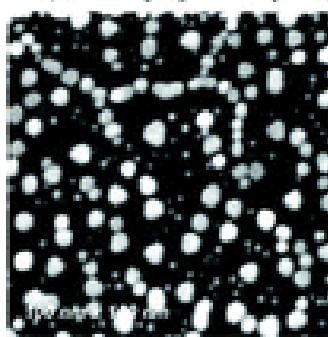
$Al_2O_3/NiAl(110)$



$Pd/Al_2O_3/NiAl(110)$



$Pd,Ca/Al_2O_3/NiAl(110)$

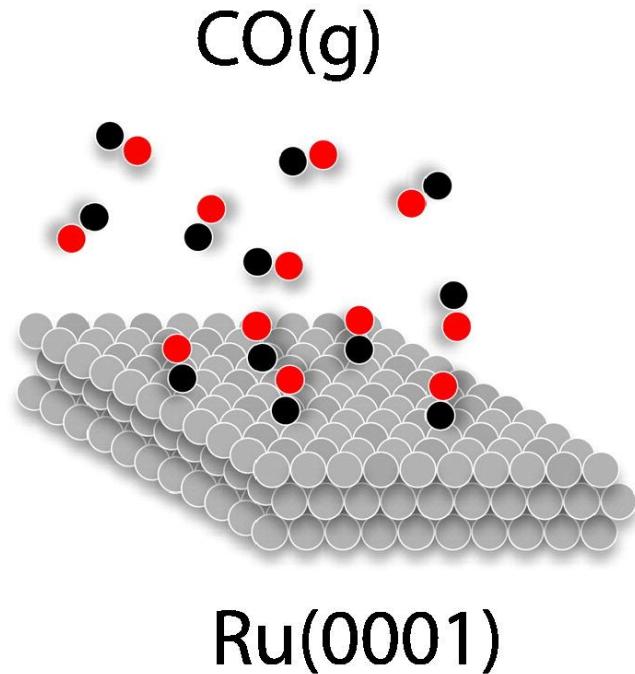


$C/Pd/Fe_3O_4/Pt(111)$

Example using AP-XPS

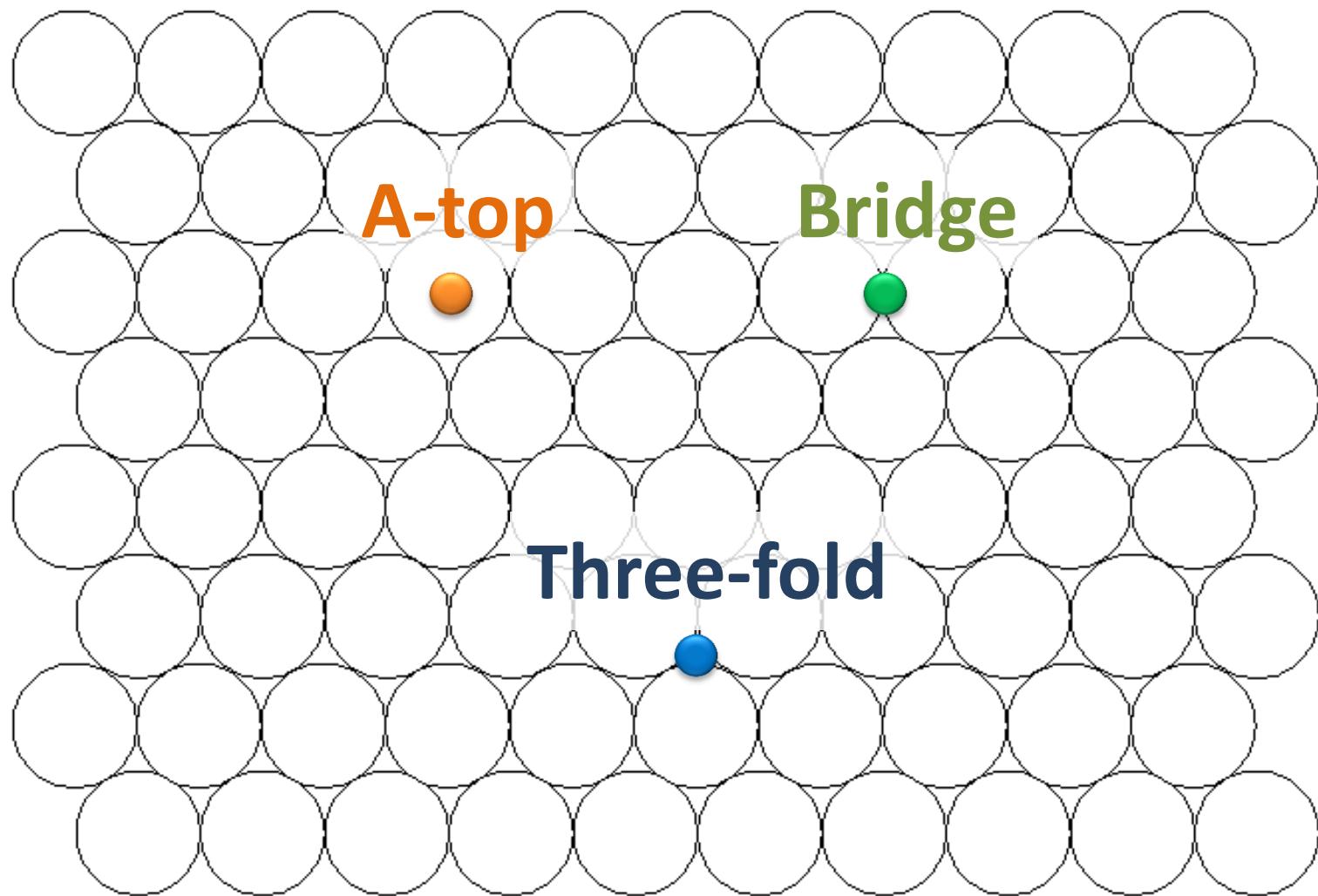
CO adsorption and dissociation on Ru(0001) at elevated pressures.

David E. Starr , Hendrik Bluhm

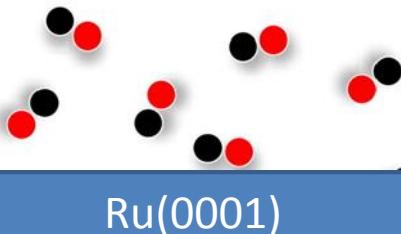


Surface Science
Volume 608, 2013, Pages 241–248

Adsorption site on triangular surface

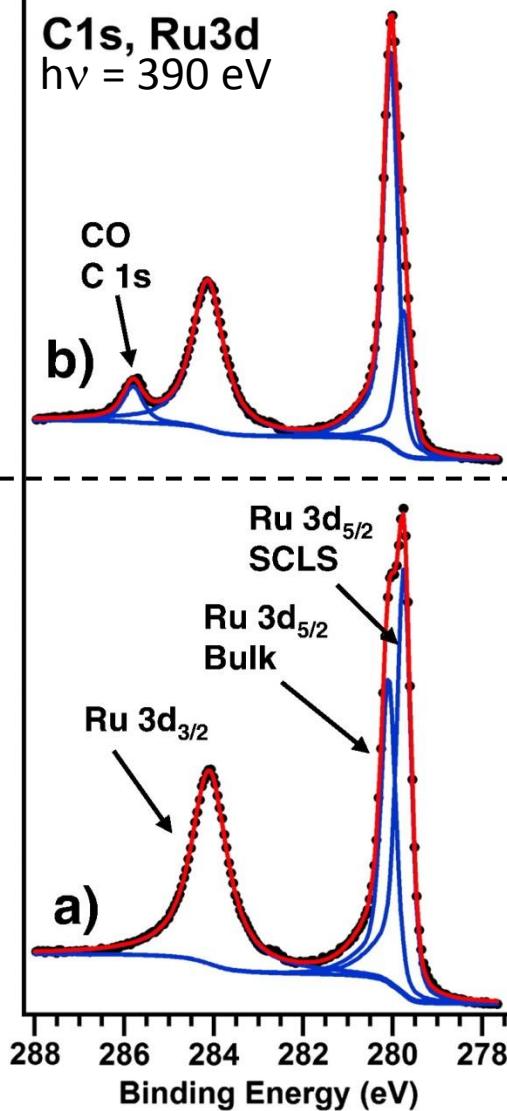


23 L of CO at 300 K

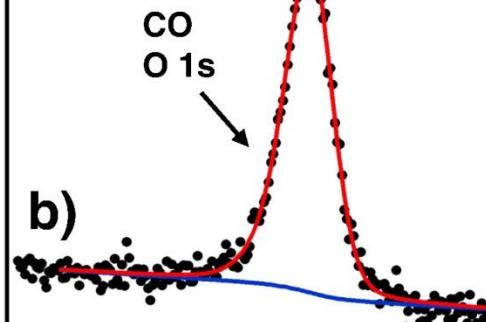


Ru(0001)

C1s, Ru3d
 $h\nu = 390$ eV



O1s
 $h\nu = 638$ eV

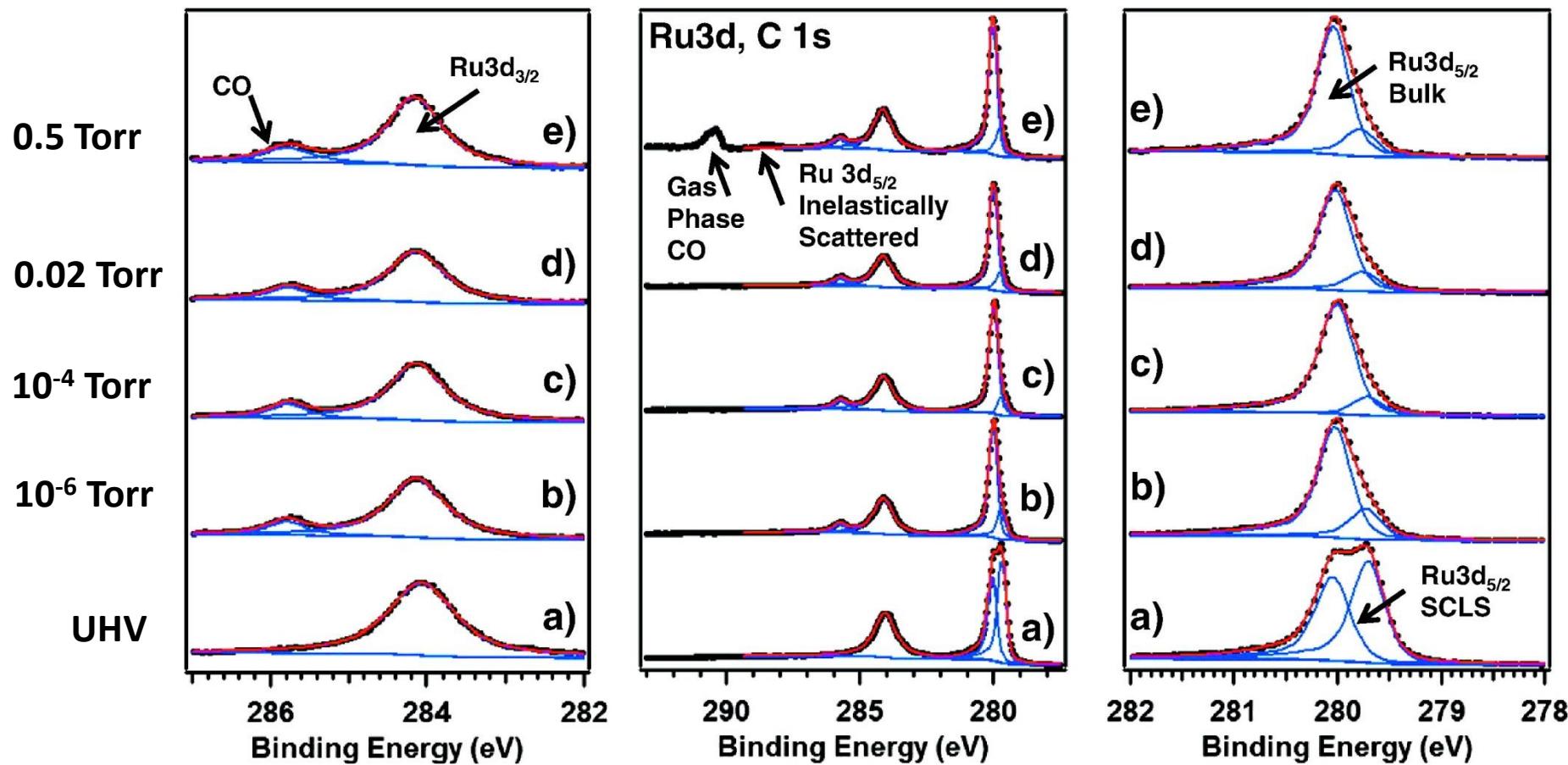


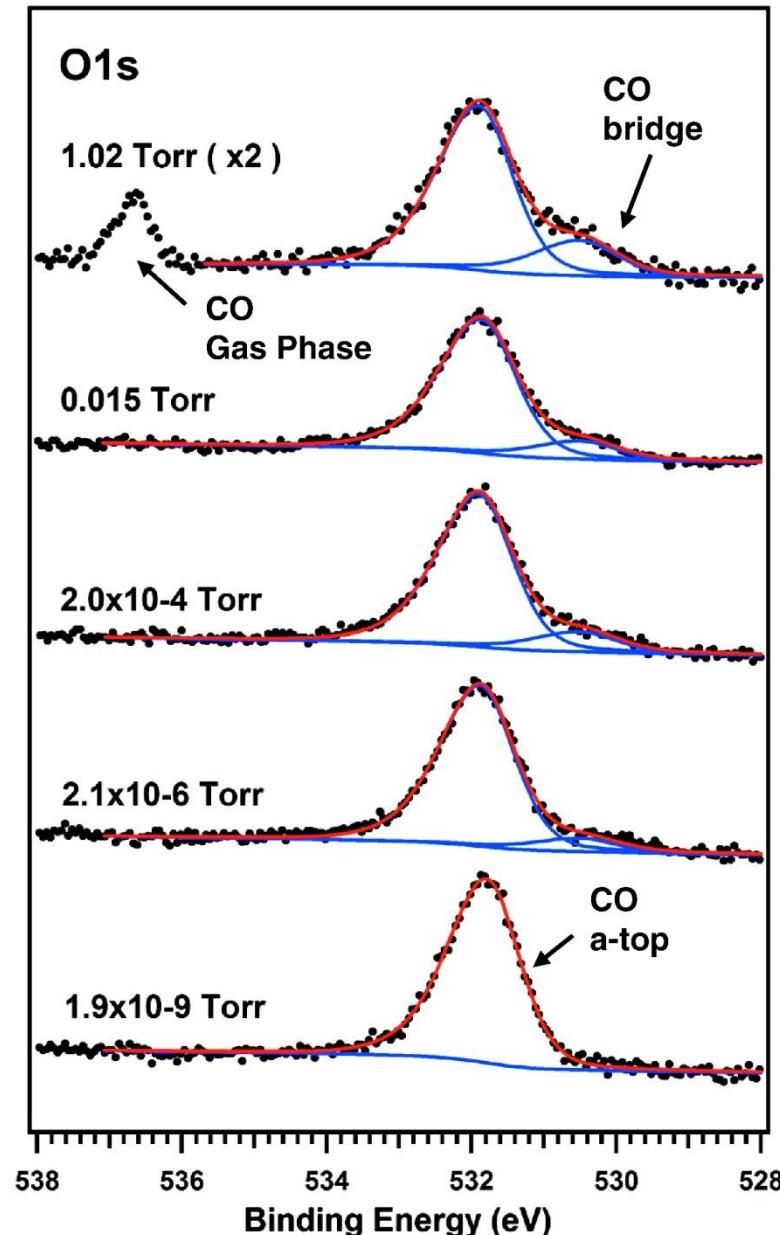
C:Ru 3d_{5/2} ratio (0.088) from the spectrum correlated to known coverage of 0.66 ML

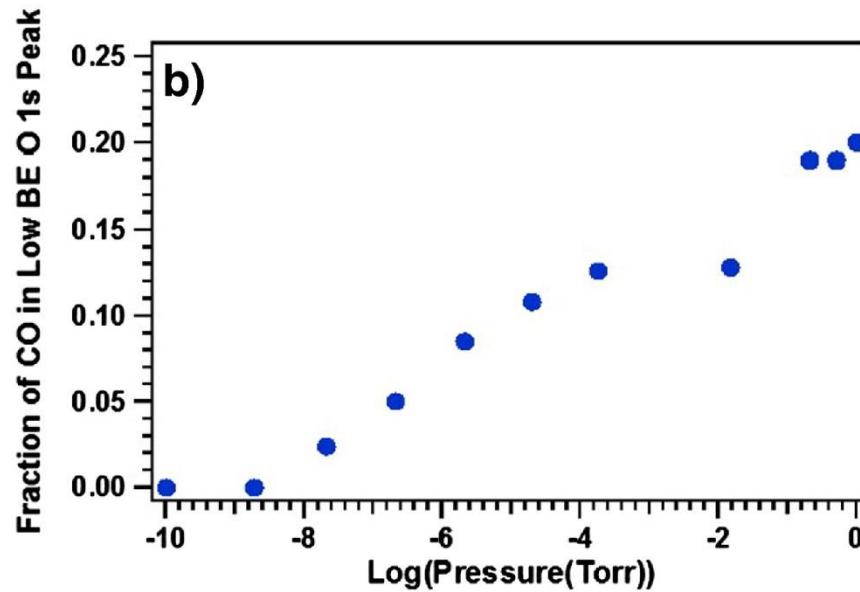
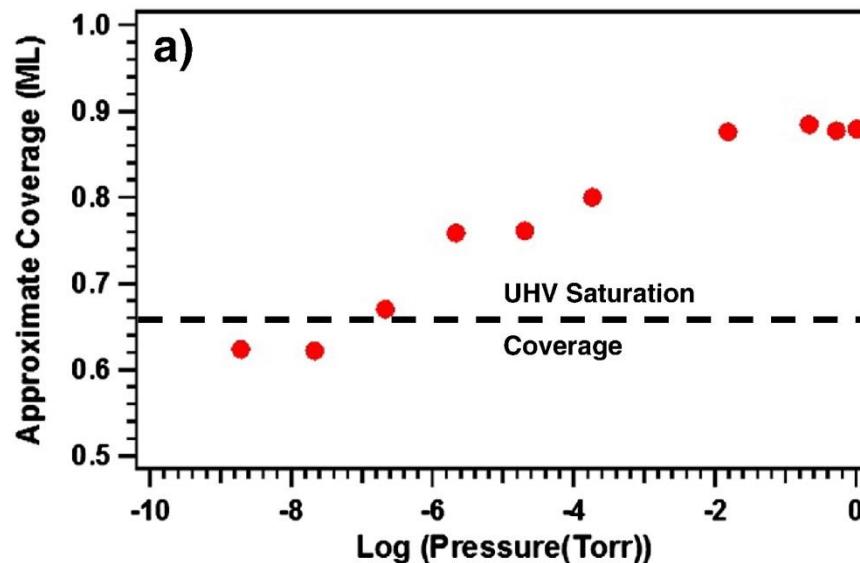
Photoionization Cross Sections. <https://vuo.elettra.eu/services/elements/WebElements.html>

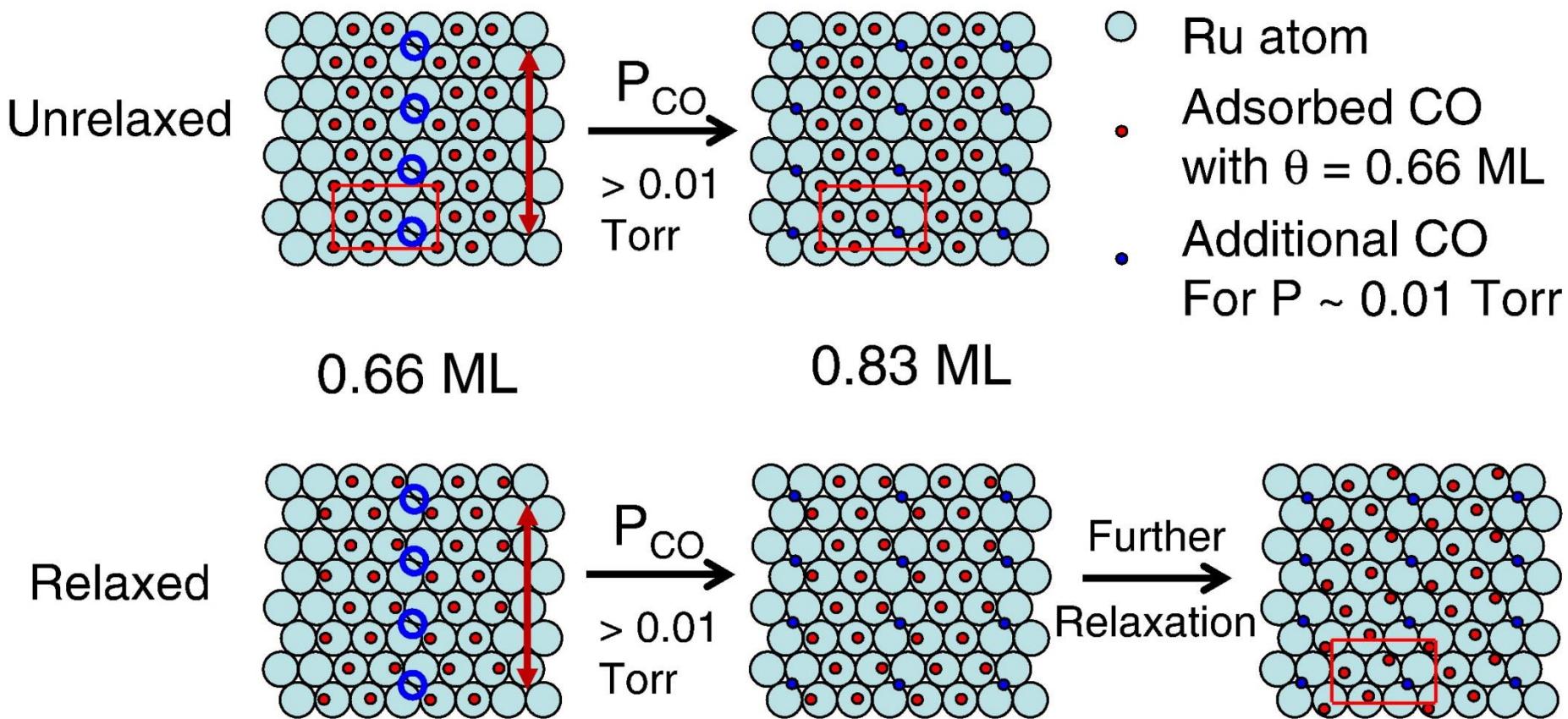
300 K

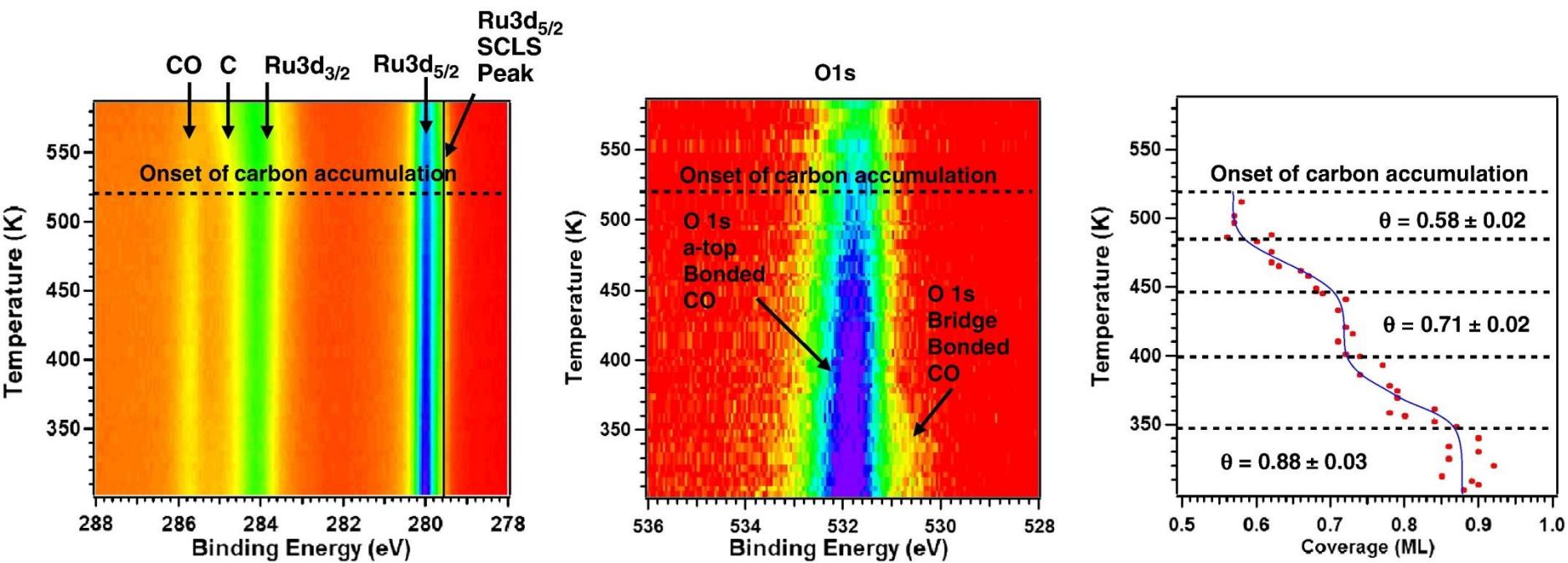
CO pressure

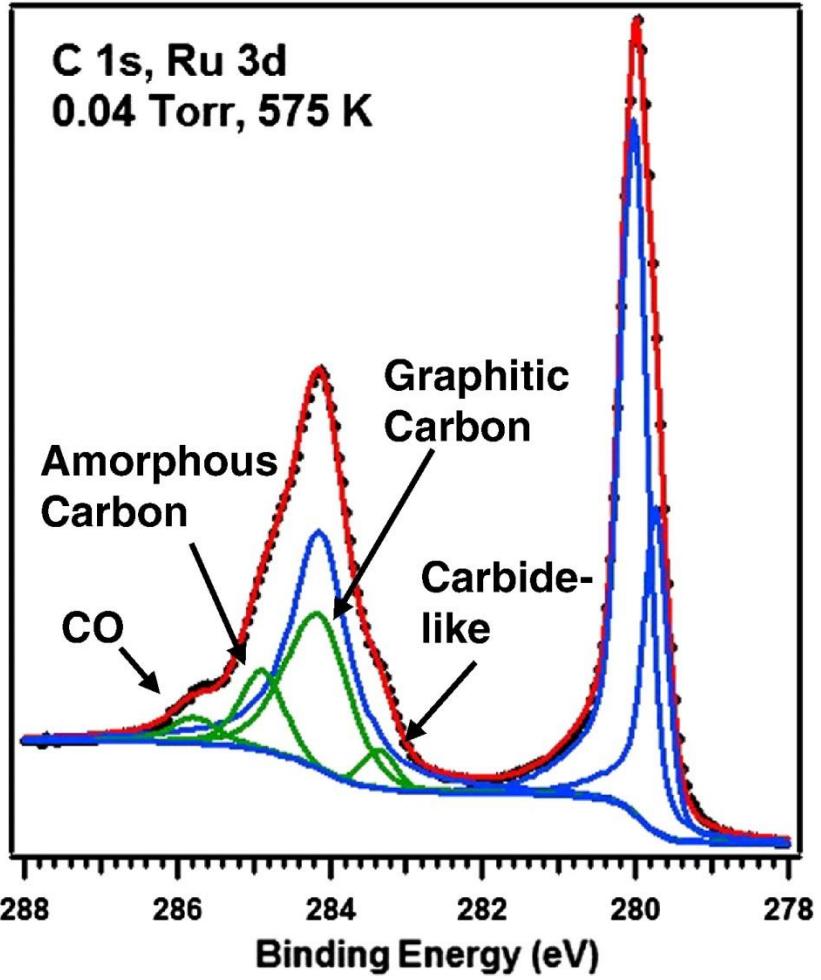
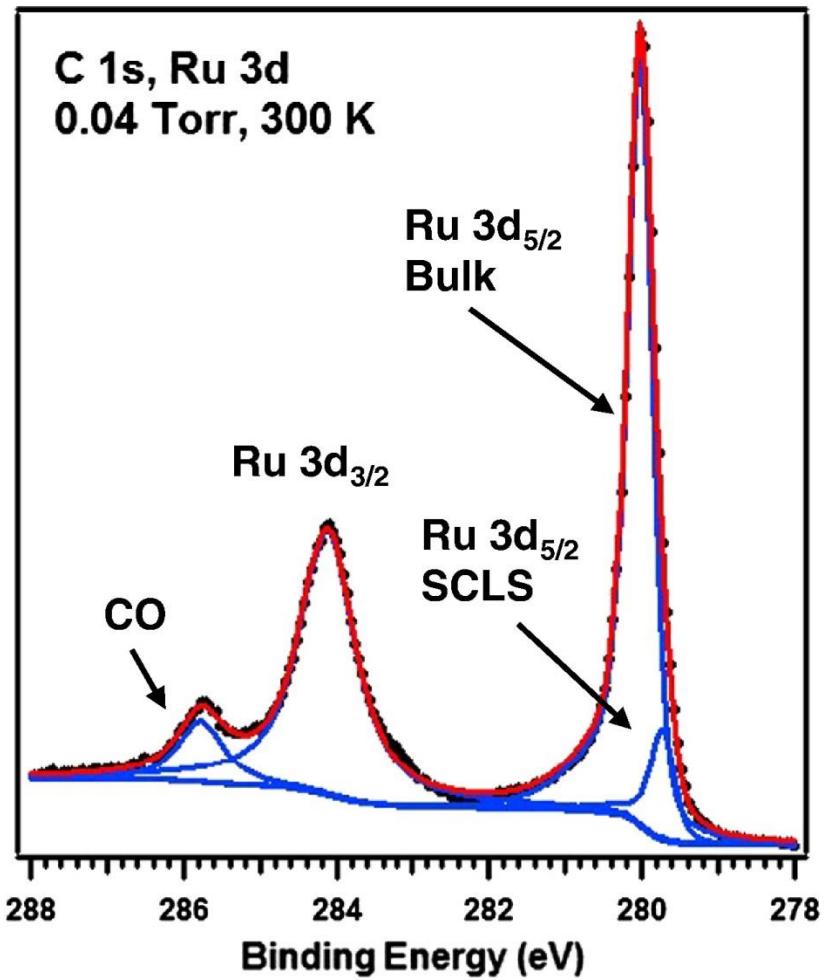




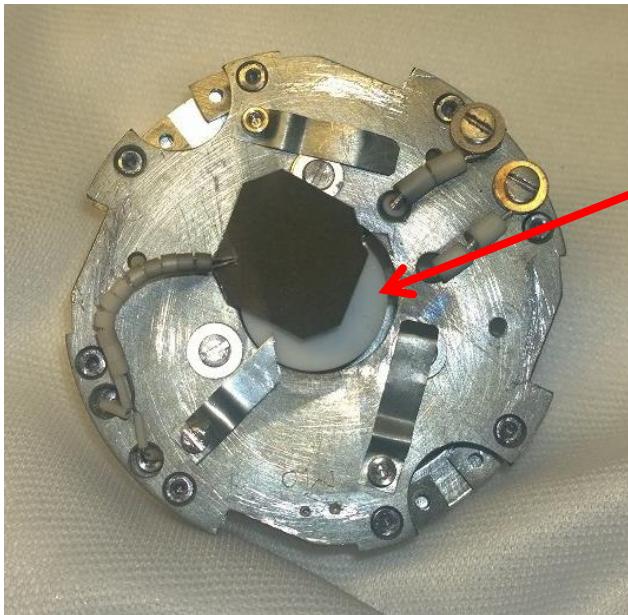






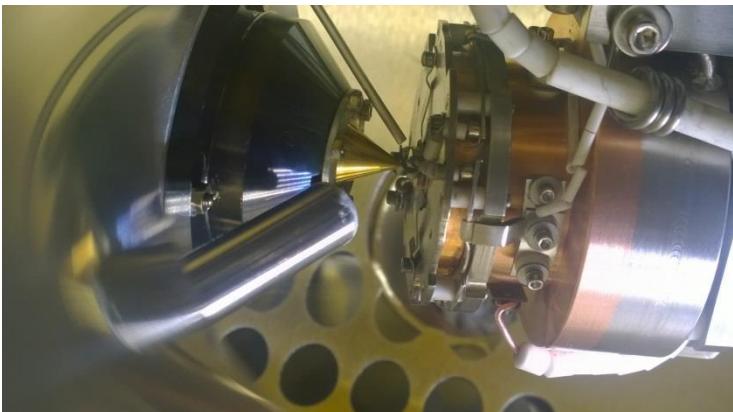


Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS) endstation at NSLS-II



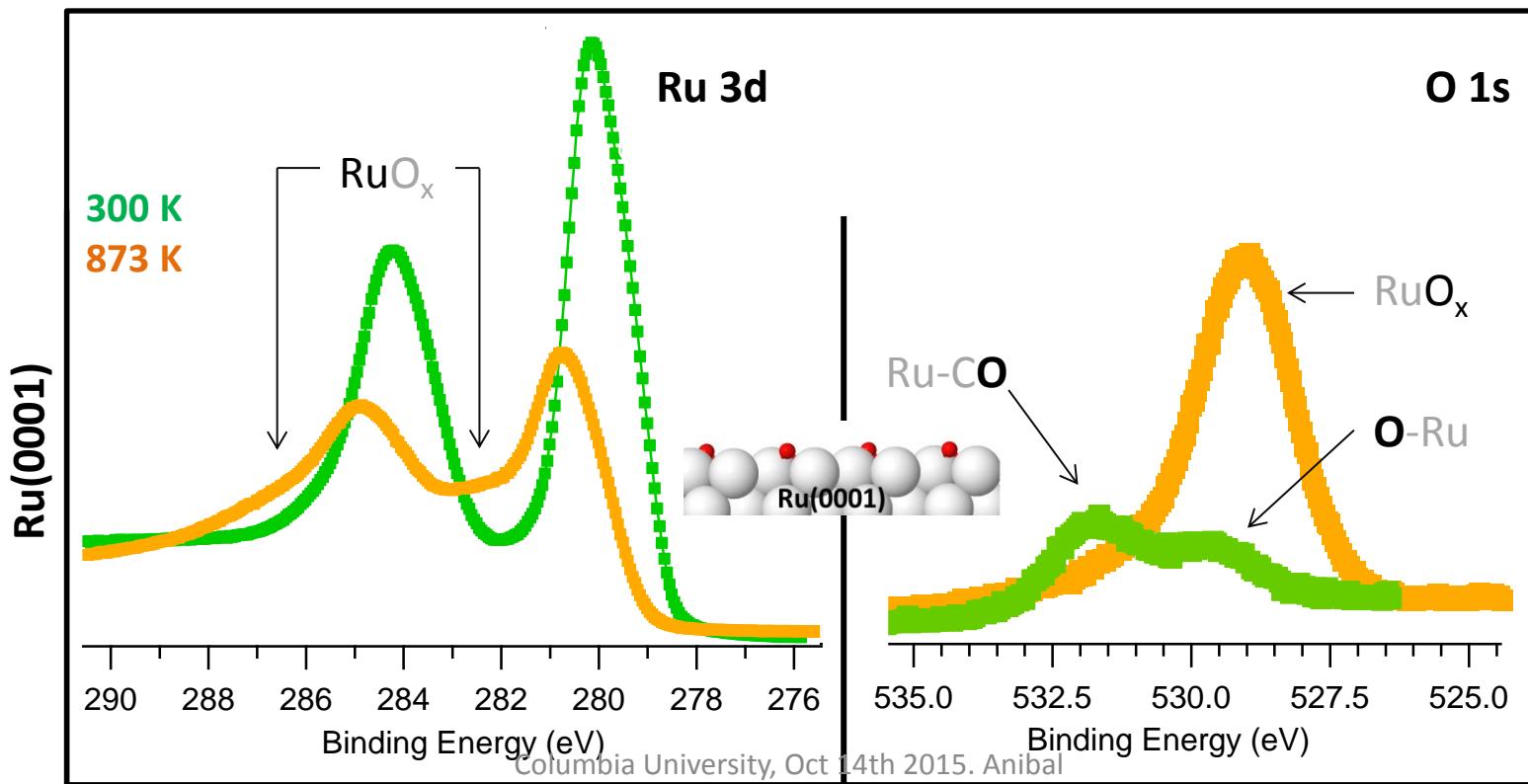
Sample goes here (up to ~ 1 cm)

- Photon Energy: 250 eV to 2000 eV
- Pressures up to 5 Torr.
- Temperatures up to 900 C
- Capillary tube into Mass Spec.
- We can dose elevated pressures of gases or liquid vapors.
- (only non-corrosive)



Exposure to elevated pressures of O₂

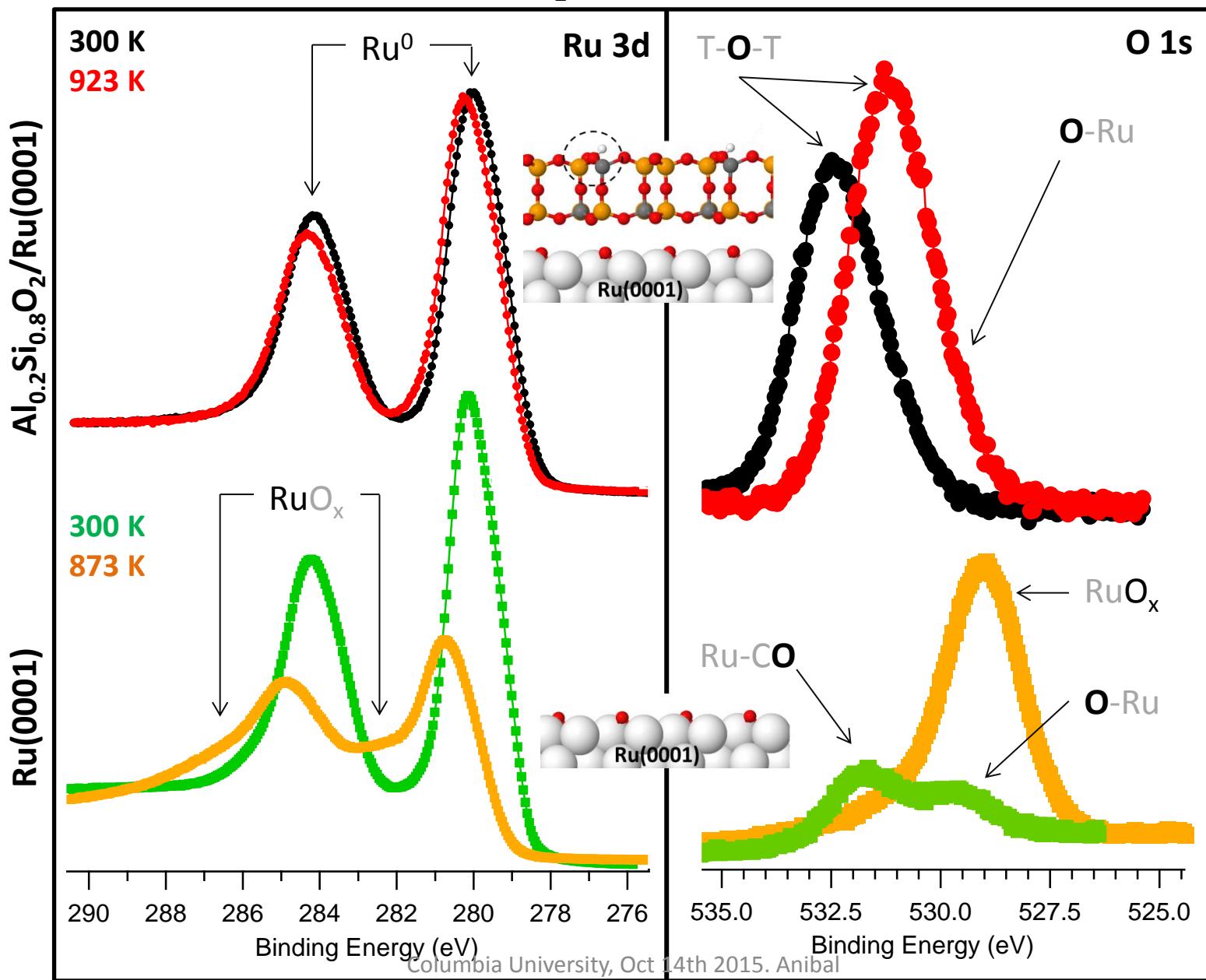
$$pO_2 = 1 \times 10^{-4} \text{ Torr}$$



Columbia University, Oct 14th 2015. Anibal

Boscoboinik - CFN, Brookhaven Lab

$$p(O_2) = 1 \times 10^{-4} \text{ mbar.}$$



Columbia University, Oct 14th 2015. Anibal

Boscoboinik - CFN, Brookhaven Lab

Useful Resources

Dynamic Periodic Table

- <http://www.ptable.com/#Orbital>

Useful XPS pages

- <http://www.xpsfitting.com/>
- <http://srdata.nist.gov/xps/Default.aspx>
- <http://xpssimplified.com/>
- <https://vuo.elettra.eu/services/elements/WebElements.html>

